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CATALYTIC FAST PYROLYSIS OF BIOMASS IN A BUBBLING FLUIDIZED BED REACTOR WITH GALLIUM PROMOTED ZSM-5 CATALYST

A Thesis Presented

by

JIAN SHI

Submitted to the Graduate School of the

University of Massachusetts Amherst in partial fulfillment

of the requirements for the degree of

MASTER OF SCIENCE IN CHEMICAL ENGINEERING

September 2012

Department of Chemical Engineering

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Approved as to style and content by:

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George W. Huber, Chair

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Williams C. Conner, Member

_____

Scott Auerbach, Member

_____

T.J.Mountziaris, Department Head

Chemical Engineering

DEDICATION

The thesis is dedicated to my parents who let their baby girl fly across the ocean to see the world.

ACKNOWLEDGMENTS

I want to acknowledge Dr. Jeff Tompsett for the help of XRD analysis of catalyst, also, my colleague Robert Coolman and Chris Gilbert for the help of biomass content analysis.

ABSTRACT

CATALYTIC FAST PYROLYSIS OF BIOMASS IN A BUBBLING FLUIDIZED BED REACTOR WITH GALLIUM PROMOTED ZSM-5 CATALYST

SEPTEMBER 2012

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Directed by: Professor George W. Huber

The huge energy demand of our society is causing fossil fuel resources to diminish rapidly. Therefore, it is critical to search for alternative energy resources. Biomass is currently both abundant and inexpensive. Biofuels (fuels produced from biomass) have the potential to replace fossil fuels if a cost effective process can be develop to convert biomass into fuels.

Catalytic fast pyrolysis is a technology that can convert biomass into gasoline ranged aromatics in a single step. By heating biomass quickly to an intermediate temperature, biomass will thermally decompose into small molecules which can fit into zeolite catalyst pores. Inside the catalyst pores, these small molecules undergo a series of reactions where aromatics are formed along with olefins, CO, CO_2, CH_4 and water. Gallium promoted ZSM-5 catalyst has been shown to promote small alkanes aromatization, thus it has the potential to increase aromatic yield in catalytic fast pyrolysis process. The focus of the thesis is to study the behavior of catalyst fast pyrolysis of biomass over Gallium promoted catalyst, and explore various ways to utilize the gas phase olefins to increase the aromatic yield.

The effect of reaction parameters (temperature, weight hourly space velocity, and fluidized gas velocity) on catalytic fast pyrolysis of biomass with Ga/ZSM-5 were studied in a fluidized bed reactor using pine saw dust as the biomass feed. The product distribution and hydrocarbon selectivity are shown to be a strong function of temperature and weight hourly space velocity. Compared to ZSM-5 catalyst at the same reaction conditions, Ga/ZMS-5 has been shown to increase the aromatic yield by 40%.

Olefins can be recycled back to the CFP fluidized bed reactor to further increase the aromatic yield. The olefin co-feeding with pine saw dust experiments indicates that co-feeding with propylene can increase the aromatic yield, however, co-feeding with ethylene will cause a decrease in aromatic yield. In both co-feeding experiments, an increase in the amount of coke formed was also observed.

Besides a simple olefin recycle, another possible way to utilize these olefins, while avoiding the high cost to separate them from other gas phase products (CO, CO_2 and CH_4),is adding a secondary alkylation unit after the fluidized bed reactor. The alkylation unit could provide a way to produce additional ethylbenzene after the main CFP process. Three zeolite catalysts (ZSM-5, Y-zeolite and Beta zeolite) were tested in the alkylation unit, and ZSM-5 catalyst shows the highest activity and selectivity in the alkylation of benzene and ethylene.

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CHAPTER 1

INTRODUCTION

Because of the huge energy demands of the modern society, global fossil fuel reserves are diminishing, and at the same time, emissions from the combustion of fossil-based fuels cause significantenvironmental problems. Searching for a renewable energy resource is the huge challenge for our society now. The use of biomass derived fuels may offer a cost effective and carbon neutral process for fuel production; it has the great potential to be the ultimate solution to our energy problem. Biomass is currently both abundant and cheap. It is estimated that current lignocellulosic biomass can provide up to 60% of the current domestic demands, at about $15 energy content equivalent per barrel. Addtionally, biofuels, are the only renewable liquid fuels[1].

Due to these advantages, the subject of biomass as the feedstock for renewable fuels has been studied worldwide. Several strategies for converting biomass has been investigated. Gasification of biomass is relatively old technology to produce syngas($CO+H_2$), which can be used for heat and electricity generation[2]. Fast pyrolysis and liquidification of biomass could be

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used for produce bio-oil[3], yields of 60-95wt % has been achieved depending on the feedstock composition[4]. Bio-oil needs to be up-graded to use as a replacement for gasoline and diesel fuels[5]. Wyman and co-workers has demonstrated that ethanol can be produced from lignocellulosic biomassby a 4 step pathway: pretreatment, enzymatic hydrolysis, fermentation and distillation[6]. These strategies all involvemultiple steps to convert biomass into fuels compatible with gasoline, though they greatly increase the cost of the process. It would be economically efficient to develop a process that convert biomass into fuels in a single step.

Catalyst fast pyrolysis is a technology that involves pyrolysis biomass in the presence of zeolite catalyst in an inert environment at atmosphere pressure. The advantage of catalytic fast pyrolysis is that it can turn biomass into gasoline ranged aromatics in a single step[7]. By heating

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[6]C. E. Wyman, *Annual Review of Energy and the Environment* **1999**, *24*, 189.

[7]1) T.R. Carlson; T.P.Vispute; and G.W. Huber; Green Gasoline by Catalytic Fast Pyrolysis of Solid Biomass-derived Compounds, (cover story)ChemSusChem (2008)

2) T.R. Carlson; G.A.Tompsett; W.C.Conner; and G.W. Huber; Aromatic Production from Catalytic Fast Pyrolysis of Biomass-derived Feedstocks, Topics in Catalysis (2009)

biomass quickly to intermediate temperatures (550-600^{o}C), lignocellulosic biomass will decompose into small oxygenated molecules[8]. These small molecules could fit perfectly into catalyst pores to form hydrocarbon pools[9] where they undergo a chain of reactions of dehydration and carbon re-arrangement. Aromatics and olefins are formed on the active sites of catalyst, and oxygen is removed in form of CO, CO_2 and H_2O. Catalytic fast pyrolysis of biomass in economic efficient for 1) it is able to convert biomass in a single reactor; 2) pretreatment of biomass is easy, only require drying and grinding; 3)itcan process a wide variety of feedstock which are abundant and cheap.

Catalytic fast pyrolysis has attracted many research due to its many advantages. Torren et al have reported when testing catalytic fast pyrolysis of glucose over different catalysts, pore size and internal volume play an important role in the aromatic yield, mid-size pore zeolite like ZSM-5 have the highest aromatic yield. (Reference).They later proved that aromatics can be produced from pine sawdust catalytic fast pyrolysis in a fluidized bed reactor with ZSM-5 catalyst directly. According to their papers, Carlson et al found out that temperature and weight hourly space velocity(defined as mass flow rate of feed per total mass of catalyst) can be used to tune both the

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3) T. R. Carlson;Y.-T. Cheng;J. Jae and G. W. Huber, Production of Green Aromatics and Olefins by Catalytic Fast Pyrolysis of Wood Sawdust, Energy and Environmental Science (2011)

[8] 1) J. B. Paine, Y. B. Pithawalla, J. D. Naworal, Journal Of Analytical And Applied Pyrolysis 2008, 83, 37.

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yield and selectivity of aromatics produced. Aromatic formation is favored at high temperature and low space velocity.Typical catalytic fast pyrolysis products include aromatics, olefins(mainly ethylene and propylene), CO, CO_2 and methane. In an effort to further increase the aromatic yield, Carlson et al have proved by recycling olefins back into reactor more aromatics could be produced. When olefins were recycled back into reactor, propylene was more active than ethylene.

Ways to increase aromatic yield of Catalytic fast pyrolysis of biomass have been investigated. One of the possible strategies is to transform the light olefins such as ethylene and propylene into aromatic hydrocarbons. Ga/ZSM-5 catalyst has been proved to help smaller alkanes undergo oligomerization into aromatics. [10](Reference 22) reported that when studying the reaction of propane aromatization, after adding Gallium to ZSM-5 catalyst, both the propane conversion and aromatics selectivity has been greatly enhanced[11]. Gallium improved ZMS-5 catalyst has shown the same effect for ethane aromatization by Monachev and co-workers[12]. After study the relationship of product distribution and propane conversion over Ga/ZSM-5, Gnep et al, concluded that Gallium species are responsible for both dehydrogenating propane as well as for naphthalene aromatization. According to Choudharry and co-workers, in order to optimize the performance of Ga/ZSM-5 towards ethylene aromatization, the catalyst should

[10] Ono Y, Transformation of lower alkanes into aromatic hydrocarbons over ZSM-5 catalyst

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possess both high acidity and optimum ratio of non-framework Gallium, which is 1:1 ratio to the strong acid sites of the zeolite catalyst[13].

There are many different methods of introducing Gallium to ZSM-5 catalyst, eg. Ion exchange, impregnation.Ga/ZSM-5 prepared by different methods does not seem to have heavy impact on catalytic behavior for isobutene aromatization[14]. Cheng et al. have compared Ga/ZSM-5 by different preparation method using furan as a model compounds for biomass and measure its conversion. The authors reported that Ga/ZSM-5 prepared by ion exchange and incipient wetness shows the highest conversion for furan and selectivity for aromatics[15]. Ono have studied the acidic property of adding Ga/ZSM-5 catalyst, and have proved there is no obvious change in both the amount acid sites and strength of them.

The purpose of this thesis is to study the behavior of catalyst fast pyrolysis of biomass over Ga promoted catalyst, and explore various ways to utilize the gas phase olefins to increase the aromatic yield. Chapter 3 emphasizes on how process parameters(temperature, Weight hourly space velocity, fluidized gas velocity) could affect the hydrocarbon selectivity, the later two chapter will discuss two different ways to utilize the olefins inside from catalytic fast pyrolysis process, by building an recycle loop or by adding an alkylation unit after the reactor.

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[13]Choudharry V, R; Devadas P; Banerjee s; Kinage A, *Micriporous and Mesoporous materials*, 47(2001)253-267

[14] Reference 15

[15]Y. Cheng, J. Jae, J. Shi, W. Fan, and G. W. Huber, Renewable Aromatics Production by Catalytic Fast Pyrolysis of Lignocellulosic Biomass with BifunctionalGa/ZSM-5 Catalysts,Angew. Chem. Int. Edit

This study could aid in designing the catalyst and overall process for catalytic fast pyrolysis of biomass.

CHAPTER 2

EXPERIMENTAL METHODS

2.1 Feedstock selection

Pine saw dust was the feed stock used in this study. It was chosen because its wide availability and cheap price. The pine saw is obtained from Amherst farm supply

The pine saw dust used in experiment is first grinded and sieved to the particle size of 0.25-1mm. Uniform particle size of the feedstock will ensure the uniform feeding rate with the auger system used in the experiment. After the biomass is grinded and sieved, it is placed inside oven at 40 ^{O}C over night to remove surface moisture content.

The elemental analysis of wood is presented in Table 1. The wood used for elemental analysis has also undergone the same treating as remove surface water. The result in table is used later on to calculate product yield. Ash content of the wood is obtained by measuring the weight difference of 1 g of dried wood after placing it in muffle furnace at 600^{o}C overnight.

Table 1: Elemental analysis of pine wood

Elemental Analysis /Wt %			
C	H	O[a]	ash
50.45	6.11	45.34	<0.005

a By Balance

2.2 Catalyst preparation

The unprompted ZSM-5 catalyst was obtained from Intercat Inc. The catalyst contains about 40% of ZSM-5, the rest is binding material to provide its mechanical property and size distribution for the fluidized bed requirement.

Ga/ZSM-5 catalyst is prepared by wetness incipient method with $Ga(NO_3)_2$ solution. The $Ga(NO_3)_2$ is obtained from (Sigma-Aldrich). 2% (weight) of Ga is added on the surface of the catalyst. Prior to the wetness incipient, the ZSM-5 catalyst is calcined at 600^{o}C for 3 hours. After wetness incipient, the catalyst is dried in oven at 110^{o}C overnight, then calcined for another 3 hours at 600^{o}C prior to the experiment.

2.3 Thermogravimetric analysis

Thermogravimetric analysis is used to analysis the cellulose, hemicelluloses and lignin content of wood. These three compounds decompose at different temperature; hemicelluloses has the lowest vaporized temperature, cellulose slightly higher and lignin is decomposing in a wide range of temperature.

Thermogravimetric analysis was performed with a Q600 TGA system. A quadruple mas spectrometer (Extrorr XT 300) was coupled via head line to the TGA to measure the volatile species. During experiment, 100ml/min of He(Air gas, 99.999%) is used to sweep the sample room to maintain inert environment. In order to avoid heat transfer limitations, a slow heating rate of 5^{o}C/min is set to ramp the temperature from room temperature to 800^{o}C, then hold for 10 minutes. After that, the sample room is cooled to 50^{o}C in 100ml/min He flow.

The TGA analysis of the pine wood used is shown in Figure 1. The small shoulder around 250^{o}C is due to hemicelluloses decomposition, the sharp peak around 300^{o}C indicates large amount of cellulose, and lignin attributes to the wide tail after that. From this result, it can be seen that the pine used in this research is composed largely of cellulose and lignin and little hemicelluloses. According to Biomass property and data base, the pine used in this study has 41.7%(weight) cellulose, 20.5%(weight) hemicelluloses and 25.9%(weight) lignin.

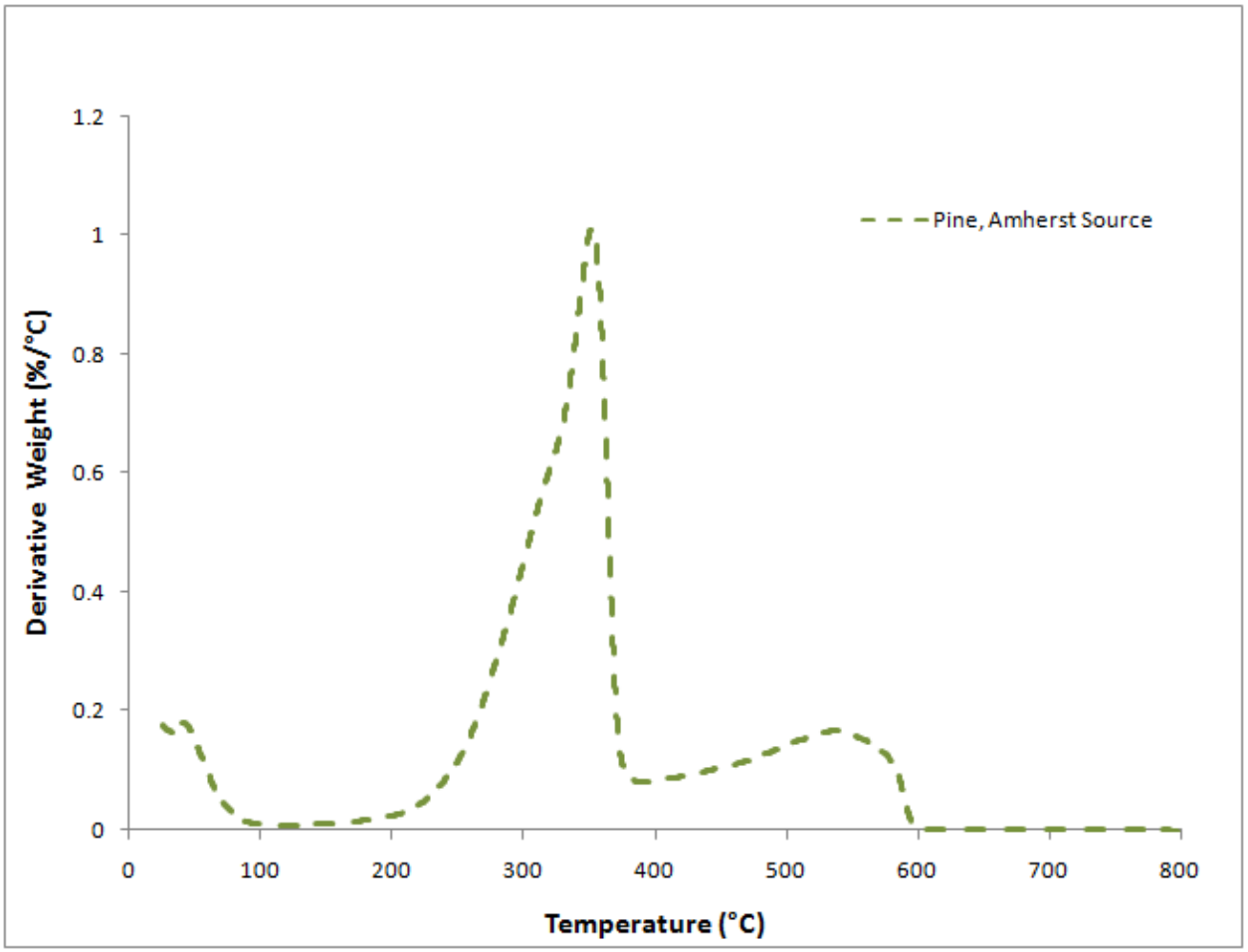

Figure 1: TGA analysis of Pine saw dust

2.4 Ammonia TPD

Alumina TPD is carried out to determine the acid sites on the catalyst. AUTOSORB®-1-MPC (Quantachrome Instruments; Boynton Beach, FL) is used for the measurement. Piror to the measurement with Alumina TPD, the catalyst is calcined at 600^{o}C for 3 hours in muffle oven to eliminate all the organic compounds. Then the catalyst is placed inside the sample chamber with 100ml/min of He (Air gas, 99.999%) flow at the temperature 500^{o}C for 2 hours to ensure all the CO_2 and moisture content absorbed on catalyst is removed. After desorption of CO_2 and water, the sample chamber is cooled down to room temperature in 100ml/min He flow. Then NH_3(Air gas, 5%(weight), He balanced) is fed into the sample room for 3 hours to ensure catalyst is fully absorbed with NH3.

After absorption, the sample room is purged at 100ml/min He for 30 minutes; then ramped to 600^{o}C at the rate of 10^{o}C/min. TCD is connected to the outlet of the sample room to record the amount of NH_3 desorbed in situ.

2.5 Elemental Analysis

Elemental analysis is carried out at Galbraith Lab, Inc(TN) for pine saw dust, fresh Ga/ZSM-5 catalyst and regenerated Ga/ZSM-5 catalyst.

As mentioned before, elemental analysis for pine saw dust is used to determine the C, H, O content. The elemental analysis for fresh and regenerated Ga/ZSM-5 catalyst is incorporated to measure the change of Ga and some trace metal amounts before and after 28 reaction cycles with biomass.

2.6 XRD

XRD analysis is done for both fresh Ga/ZSM-5 catalyst and regenerated catalyst to investigate the crystal structure change of catalyst after reaction cycles. XRD analysis is carried out on RigakuMSC RU-H3R X-ray generator and RAXIS 4++ X-ray detector equipped with Osmic Confocal Max-Flux optics.

2.7 Fluidized bed

Catalytic fast pyrolysis (CFP) of pinewood was conducted in a fluidized bed reactor. The fluidized bed reactor is 2-in in diameter, 10-in in height and is made of 316 stainless steel. Inside the reactor, the catalyst bed was supported by a distributor plate made of stacked 316 stainless mesh (300 mesh). Before each reaction, the catalyst is first calcined at 600^{o}C in-situ, then cooled down to the reaction temperature in He flow.

The solid biomass (pinewood) was introduced into the reactor from a sealed feed-hopper. Prior to the run, the pinewood was grinded and sieved to a particle size of 0.25 – 1 mm. During the reaction, the catalyst was fluidized by helium gas which was flowing at 800 sccm to enable the reactor operates at bubbling fluidized bed flow regime. The hopper was continuously purged by helium at 200 sccm to maintain an inert environment. Both the reactor and the inlet gas stream were heated to reaction temperature (550 ^{o}C).

After the reaction, the effluent flowed through a cyclone to remove solid particles, including small catalyst and char. The effluent then flowed into 7 condensers in series to separate liquid

and gas phase products. The first 3 condensers were placed in an ice-water bath with ethanol inside as a solvent, and the other 4 condensers were surrounded by a dry acetone bath (-55^{o}C) without solvents. Finally, the uncondensed gas phase products were collected in air bags. The reaction time was 30 min. After reactions the reactor was purged by 1000 sccm helium for 30 minutes to make sure that the only products remained inside the reactor was coke. Liquid products are extracted from condensers by ethanol. Total volume of liquid is recorded.

The catalyst was regenerated by air at 800 sccm for 3 hours. During the regeneration, the effluent passed through a copper converter in which CO was converted into CO_2, and the CO_2 was trapped by a CO_2 trap. Gas phase products were analyzed by a GC-FID/TCD (Shimadzu 2014). Liquid samples were analyzed by a GC-FID (HP 7890). Coke yield was obtained by analyzing the weight change of the CO_2 trap.

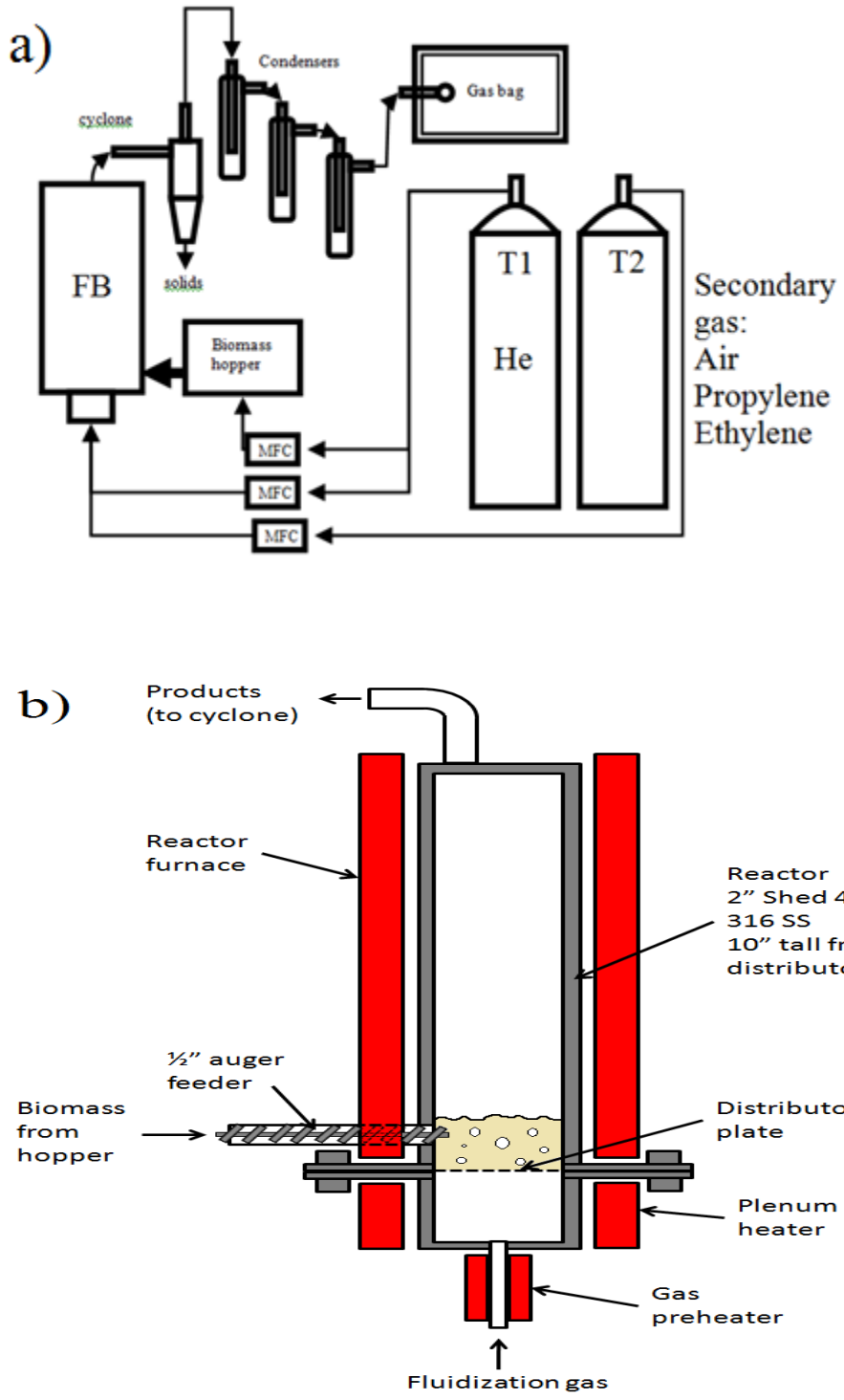

Figure 2: Fluidized bed reactor set-up a) Schematic of fluidized bed system, b) Detailed drawing of the reactor (Picture courtesy to Torren Calson)

CHAPTER 3

CFP OF BIOMASS WITH GA/ZSM-5 CATALYST

3.1 Time on Stream for biomass conversion over Ga/ZSM-5 catalyst in fluidized bed reactor

Figure 1 shows the gas concentrations as a function of time olefins, CO, CO_2, CH_4 of pinewoods conversion over Ga/ ZSM-5 catalyst at 550℃. Zeolite catalyst used in CFP process usually deactivates in less than one hour because of coke deposition onto the catalyst. In this study, all experiments are run for 30 minutes.

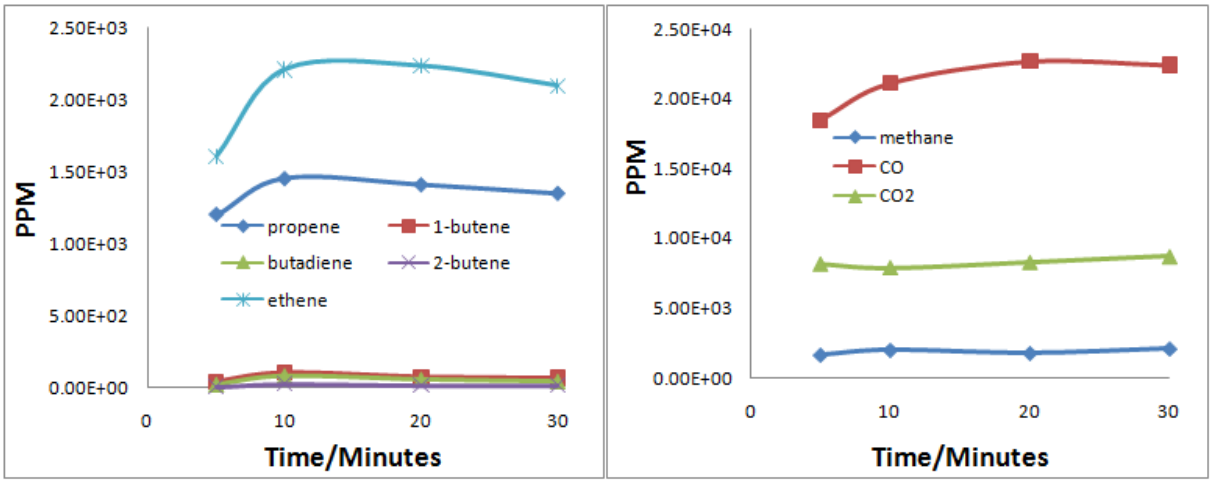

Figure 3: Gas concentration as a function of time for biomass conversion over Ga/ZSM-5 catalyst. Reaction condition: 550^{o}C, WHSV 0.35hr^{-1} and He flow rate 1000 sccm

According to Figure 3, the gas product concentration shows no signs of decreasing in 30 minutes of experiments. The olefins(ethylene, propylene, butane and butadiene) concentrations generally increase between the start of reaction to 10 minutes and then very slowly decrease. The

increase of gas product before 10 minutes can be explained by the formation of hydrocarbon pool in the active sites catalyst. Olefins and aromatics are both formed from the hydrocarbon pools inside catalyst. After biomass enters the reactor, it first undergoes thermal decomposition to form anhydrous sugar. When the anhydrous sugar come in contact with the catalyst, the hydrocarbon pools are formed on the surface of the catalyst. The shift from increasing of gas product concentration to a slow decrease could indicate that the hydrocarbon pools are fully developed after 10 minutes after reaction. The slow decrease of olefins concentration after 10 minutes is likely to be result of the coke formation on Ga/ZSM-5 catalyst. Because the change of olefin concentration after 10 minutes is very small, Ga/ZSM-5 catalyst is stable for 30 minutes of experiments.

CO, CO_2 and methane have different trends in the 30 minutes of reactions. CO_2 concentrations show a slow increase trend after 10 minutes as the olefin concentrations begin to drop. Also, $CO_2$is at its minimum value around 10 minutes while olefins concentration maximize around that time.

3.2 Effect of reaction temperature for biomass conversion over Ga/ZSM-5 catalyst

Table 2 shows the detailed carbon yield and selectivity for biomass conversion over Ga/ZSM-5 catalyst at different temperatures. The product distribution of CFP is a strong function of temperature

Table 2: Detailed carbon yield distribution and product selectivity for CFP of Wood over Ga/ZSM-5 catalyst as a function of temperature. Reaction Condition: Ga/ZSM-5 catalyst, biomass WHSV 0.35hr-1 , He velocity 2.27cm/s, reaction time 30minutes.

	Temperature(℃)			
	450	500	550	600
Overall Carbon Yield(%)				
Aromatics	6.63±0.78	18.41±0.85	23.17±0.97	17.53±0.98
Olefins	4.09±1.87	7.05±0.67	8.90±4.21	6.62±4.90
Methane	0.60±0.06	1.07±0.11	1.50±0.13	2.82±0.04
CO_2	4.77±0.72	5.30±0.04	5.41±1.00	4.49±0.90
CO	13.42±0.95	15.58±0.70	17.15±0.14	17.21±0.44
Coke	64.39±1.43	40.79±0.80	33.25±1.81	37.64±3.30
Total	93.89±2.34	88.19±1.40	89.35±2.13	86.31±3.50
Aromatic Carbon Selectivity(%)				
Benzene	12.58±1.63	19.15±1.82	20.00±0.36	26.79±1.67
Toluene	29.58±1.55	39.18±2.02	26.41±1.79	24.89±2.20
P-xylene	15.27±0.79	11.30±1.30	7.39±0.67	4.86±1.23
M-xylene	11.52±0.52	8.73±0.76	5.57±0.89	4.01±0.43
O-xylene	2.20±1.21	3.31±1.34	5.51±1.10	1.35±0.89
Ethyl-benzene	3.54±0.54	1.02±0.32	2.57±0.79	0.71±0.29
Styrene	0	0.61±0.06	2.19±0.16	2.06±0.10
Phenol	0.65±0.25	0.87±0.11	0.98±0.34	0.98±0.25
Benzofuran	7.07±0.19	1.45±0.46	1.30±0.18	1.60±0.32
Indene	1.63±0.48	0.51±0.54	1.15±0.64	0.29±0.21
Naphthalene	8.58±1.37	15.14±1.94	6.35±0.66	11.58±1.78
2-Methyl Naphthalene	7.52±0.11	4.67±0.96	4.63±0.02	1.2±0.03
Olefin Carbon Selectivity(%)				
Ethylene	28.36±2.82	34.05±1.51	42.53±4.91	43.71±3.26
Propylene	54.52±1.69	49.18±0.54	49.11±2.83	41.73±1.23
Butene	12.29±0.43	7.10±0.56	2.61±2.40	3.44±2.40
Butadiene	4.89±1.23	9.68±1.54	5.73±4.51	4.19±3.21
A+O Carbon Yield/ Theoretical A+O Carbon Yield(%)				
	13.92±3.34	34.32±2.00	42.65±5.95	29.46±3.88

It is noticeable that temperature has extensive effect on the amount of coke formed in experiments. The coke formation decreases by half by when the temperature increases from 450 to 550^{o}C. For CFP process, coke formation is the major competing reaction for aromatics and olefin formation.

Table 2 shows that the aromatic and olefin yields peak at 550^{o}C when the space velocity is kept constant at 0.35hr^{-1}. As can be seen in the table, below 550^{o}C coke formation dominates all the other reactions. Therefore, by raising the temperature, the coke amount is reduced, and other products yield is increased. If the reaction temperature continue rise to 600℃ then the alkylation reaction, which is exothermic, becomes thermodynamically unfavorable. The larger aromatic molecules de-alkylate to form smaller aromatics and olefins, which reduce the aromatic yield. As presented in the table, at higher temperature region of 500-600^{o}C, the larger aromatic molecule, eg, toluene, xylene, ethylbenzene all decrease with the increase of temperature. Ga/ZSM-5 catalyst is chosen because it helps olefin oligomerization to form aromatics. Larger olefins like propylene are easier to form aromatics compare to ethylene, because less reaction steps are required. Thus the reducing of larger olefin could also contribute to the decrease of aromatics.

P-xylene is an important chemicals which can be used as precursor for terephthalic acid and dimethyl terephthalate, both monomers used in the production of polyethylene terephthalate (PET) plastic bottles and polyester clothing. In CFP process, xylene may be formed by aromatics alkylation with olefins and oligomerization reaction. At high temperature, the xylene oligomerization is thermodynamically restricted. From thermodynamic calculation, at 800K, the equilibrium product from xylene oligomerization reaction is m-xylene(46%), O-xylene(21%), P-

xylene(22%), ethylbenzene(11%). Table 2 shows we have achieved a higher percentage of P-xylene production than the equilibrium ratio. The p-xylene yield is higher than both the o& m-xylene. ZSM-5 catalyst have been shown to promote oligomerization reaction for m&o-xylene to form p-xylene. This expeirment result may suggest that CFP process for biomass coversion have the potential to produce p-xylene.

The yield of CO, CO2 is not significantly affected by temperature at the region of 500 to 600℃. The lack of sensitivity of CO and CO2 yields to the temperature indicates their formation undertook different pathways compare to olefins and aromatics. Notably, other gas form product, CH_4, its carbon yield increase with the temperature. The reason to that is CH4 may have been produced from water gas shift reaction, which is an endothermic reaction favorable at higher temperatures.

3.3 Effect of Space velocity for biomass conversion over Ga/ZSM-5 catalyst

Table 3: Detailed carbon yield distribution and product selectivity for CFP of Wood over Ga/ZSM-5 catalyst as a function of biomass WHSV. Reaction Condition: Ga/ZSM-5 catalyst, 550℃,He fluidization velocity 2.27cm/s, reaction time 30minutes.

	WHSV(hr^{-1})					
	0.1	0.35	0.62	0.98	1.19	1.63
Overall Carbon Yield (%)						
Aromatics	10.07	23.17	20.17	14.02	12.53	9.20
Olefins	11.35	8.90	9.42	7.07	7.91	5.77
Methane	0	1.50	3.69	2.61	3.27	3.25
CO_2	13.80	5.41	8.16	5.67	6.71	4.71
CO	12.07	17.15	26.10	19.28	21.77	16.06
Coke	34.31	33.25	39.55	38.23	34.53	45.66
Total	81.60	89.35	107.10	86.88	86.72	84.65
Aromatic Carbon Selectivity (%)						
Benzene	20.31	25.74	18.48	12.94	17.22	15.69
Toluene	29.27	33.99	33.52	32.59	42.39	33.09
Xylenes	14.69	23.77	17.56	18.36	24.52	19.25
Ethyl-benzene	1.31	3.31	3.81	2.75	3.46	3.61
Styrene	2.53	2.82	3.97	3.69	5.98	7.13
Phenol	0.63	1.26	0.73	0.75	0.07	0.06
Benzofuran	6.63	1.67	3.90	3.22	4.61	1.56
Indene	0.49	1.48	2.19	0.53	0.95	0.97
Naphthalene	15.85	5.96	9.00	12.42	6.58	10.32
2-Methyl Naphthalene	7.84	3.16	4.78	0.15	0.19	8.15
Olefin Carbon Selectivity (%)						
Ethylene	0	42.53	34.5	35.69	35.16	41.71
Propylene	97.76	49.11	52.74	43.73	51.54	46.07
Butene	2.00	2.61	4.15	15.28	8.08	6.41
Butadiene	0	5.73	8.18	5.3	5.25	0.16
A+O carbon yield/theoretical A+O carbon yield (%)						
	14.83	42.65	37.47	26.54	27.39	19.44

The study of WHSV on biomass conversion is all conducted at the temperature of 550℃, the temperature shows higher aromatic and olefin yield at low space velocity. WHSV is defined as the mass flow rate of the fed divided by the mass of catalyst inside the reactor.

The experiment results of WHSV of CFP of pine sawdust are shown in Table 3. Changing the WHSV has large impact on the product distribution. Unlike temperature which tunes the distribution of products by affecting the amount of coke formed, WHSV have less obvious effect on coke. On the other hand, products like CO, CO_2 which are not sensible to temperature, change correspond to WHSV. By increasing WHSV of biomass, CO_2 shows a decreasing trend while CO generally shows a raise trend. Although CO_2 and CO and bothare formed by CFP of pine sawdust, their different response to WHSV may indicate they have different formation mechanism.

Table 3 also revealed a general trend of biomass conversion. At very low space velocity($0.1hr^{-1}$), smaller molecular like olefins, CO_2, CO, dominates the distribution, while at high WHSV, coke which is highly polymerized form of carbons, dominates the product distribution. Aromatics' yield peak at $0.35hr^{-1}$, and decrease at too low and at high WHSV. This trend may be explained by the hydrocarbon pools formed at the surface of the catalyst. If there is too little biomass is supplied to the catalyst, because of the decarbonizes function of Ga and also because molecular inside the hydrocarbon pools have too little chance to interact with each other to form larger product, smaller moleculars tends to be produced from the hydrocarbon pool. When there are enough biomass is provided to the catalyst, the hydrocarbon pool is more saturated and molecular has more chance to interact with each other to form larger product. The aromatic yield maximized at this point. When too much biomass is sent into the reactors, the

catalysts do not have enough active sites to capture all theprolysis vapor, this could lead to decrease of aromatic yield. When operating at high space velocity, there is larger percent of coke formed on the surface of the catalyst, which could lead to quick deactivation of catalyst. This could also leads to decrease in aromatic yield.

Compared to experiments results with biomass conversion over ZSM-5 catalyst at different WHSV and 600oC, the aromatic yield peaks at 0.35hr-1 and decrease at too high and too low space velocity. This trend can be explained by the same amount of active sites on both catalysts.

3.4 Effects of carrier gas velocity for biomass conversion over Ga/ZSM-5 catalyst

The fluidized bed is widely used in industry for rapid heat transfer and ability to use very small catalyst. Inside a fluidized bed reactor, the gas velocity is sufficient to suspend the catalyst particles, but not large enough to carry them out of the vessel. By changing the carrier gas velocity, there are four regimes in which to operate fluidized bed. Smooth region occurs when the reactor is operating at minimum fluidized velocity. The minimum fluidized velocity can be calculated theoretically according to reactor size, catalyst particle size and fluidized gas characterizes, or can be measured experimentally. Further increasing the gas velocity will cause instability, and some of the gas starts by passing the catalyst bed inform of bubbles. This region is called bubbling regime. It usually appears when operating at 3 times minimum fluidized velocity. If the gas velocity is increased further, then the fluidized bed will be operated in slugging regime. Inside this region, there will be slug flow inside the reactor which will result in

unstable chaotic operation. Continue to increase the gas velocity will eventually result in the catalyst particle being carried out the reactor bed.

Changing the fluidized gas velocity could potentially change the fluidized dynamics inside the reactor. He is used as fluidized gas for all the experiments inside this study. Table 4 present the results of a series experiment performed at different He flow rate. All the experiments for He flow rate are performed at 550℃ and 0.35hr-1. According to our calculation, the minimized fluidized velocity for the reactor used in experiment is 690 sccm.

Table 4: Detailed carbon yield distribution and product selectivity for CFP of Wood over Ga/ZSM-5 catalyst as a function of fluidization gas velocity . Reaction Condition: Ga/ZSM-5 catalyst, 550℃, biomass WHSV 0.35hr-1, reaction time 30minutes.

	Gas Velocity(cm/s)		
	1.92	2.26	3.16
Overall Carbon Yield(%)			
Aromatics	24.27±1.22	23.17±0.97	22.83±6.89
Olefins	5.84±2.23	8.90±4.21	7.27±3.87
Methane	1.62±0.55	1.50±0.13	1.12±0.40
CO_2	4.73±0.65	5.41±1.00	4.37±2.00
CO	17.24±3.23	17.15±0.14	11.85±4.96
Coke	33.44±2.23	33.25±1.81	35.89±3.25
Total	87.14±1.67	89.35±2.13	83.31±0.12
Aromatic Carbon Selectivity(%)			
Benzene	18.48±4.67	20.00±0.36	32.53±7.96
Toluene	31.85±1.14	26.41±1.79	27.02±0.13
Xylenes	16.71±2.23	18.47±3.67	5.67±4.29
Ethyl-benzene	7.84±1.34	2.57±0.79	3.59±2.21
Styrene	2.43±0.67	2.19±0.16	3.64±0.02
Phenol	2.88±0.56	0.98±0.34	5.64±1.12
Benzofuran	4.94±0.18	1.30±0.18	4.29±0.23
Indene	2.34±1.95	1.15±0.64	2.48±2.76
Naphthalene	7.05±1.40	6.35±0.66	4.70±5.01
2-Methyl Naphthalene	4.52±0.54	4.63±0.02	1.23±0.03
Olefin Carbon Selectivity(%)			
Ethylene	29.40±3.38	42.53±4.91	42.33±7.60
Propylene	59.20±3.73	49.11±2.83	59.68±7.00
Butene	4.07±1.94	2.61±2.40	3.13±0.89
Butadiene	7.52±2.64	5.73±4.51	2.22±0.30
A+O Carbon Yield/ Theoretical A+O Carbon Yield(%)			
	39.11±5.49	42.65±5.95	39.09±6.70

According to Table 4, total carbon yield for aromatics, methane, CO, CO_2 and coke stay almost the same at He flow rate region chosen for the experiment. Only olefins yield shows a slight peak gas velocity of 2.26cm/s, while decrease a little in smooth and slugging region. It is notable that the larger the gas velocity, the shorter the residence time of reactants inside the reactor. This result may indicate in the flow rate region tested, increase the time pyrolysis vapor stay in contact with catalyst does not necessarily increase the aromatic yield. Compared to overall carbon yield for each group of products, the gas velocity has more effect on the aromatics selectivity. Benzene selectivity increases from 18.48% to 32.53% with the increase of gas velocity. This may due to benzene is leaving reactor too quickly before it can alkylate with olefins to produce heavier aromatics.

Although increase gas velocity does not seem to have much effect the product distribution and aromatics yield, it may help remove the char and ash produced from the biomass. According to Yu-chuang Lin ect's paper, char formation could both heterogeneously on the surface of catalyst and homogeneously inside the gas phase. Ash is the nature product of biomass pyrolysis, it may contain various kinds of mineral like Magnessium, Calcliumect. Increasing gas velocity could reduce the residence time of char and ash inside the reactor and help remove them from the system. Accumulating of char and ash inside the system may cause blockage inside the reactor. Thus increase gas velocity to help remove char and ash may help long-term steadily operation of the system.

3.5 Comparison between Ga /ZSM-5 catalyst and ZSM-5 catalyst

As mentioned before, Ga/ZSM-5 catalyst is chosen for the biomass conversion experiments based on its ability to promot olefin aromatization. Because olefin accounts for about 8% of the carbon yield for biomass conversion over ZSM-5, it is expected Ga/ZSM-5 catalyst could increase aromatic yield.

Table 5 present the experiment results of both catalyst at 550 and 660^{o}C and He flow rate of 1000sccm. Compare to ZSM-5 catalyst, Ga/ZSM-5 catalyst shows obvious increase in aromatic yield at both experiment conditions. With ZSM-5 catalyst alone, the highest yield we achieved is 15.4%, while with Ga/ZSM-5 catalyst, the highest yield is 23.2%. While the aromatic yield differs greatly between the two catalysts, the aromatic species produced are basically the same. Benzene, toluene, xylene are three main aromatic product by both catalyst. These three chemicals accounts for more than 80% of aromatic produced over both catalysts. It can be explained by the character tics of Ga/ZSM-5 catalyst. According to research papers, the main products from olefin aromatization on Ga/ZSM-5 catalyst are benzene and toluene. It is notable that benzene, toluene and xylene are the three aromatics which have wider application in industry than the other aromatics produced. This means Ga/ZMS-5 increase the aromatic yield greatly without sacrificing the value of the products.

Table 5: Detailed comparison of product distribution and selectivity of pine woods reacting over ZSM-5 and Ga-ZSM-5 catalysts. Reaction Condition: WHSV 0.35hr-1, He flow rate 1000sccm, reaction time 30 minutes.

Catalyst	ZSM-5	Ga-ZSM-5	ZSM-5	Ga-ZSM-5
Temperature (℃)	550	550	600	600
Overall Carbon Yield(%)				
aromatics	15.4	23.2	11.5	17.5
olefins	7.1	8.9	8.8	6.6
methane	2	1.5	2	2.8
CO_2	7.7	5.4	4.7	4.5
CO	20.3	17.1	24.9	17.2
coke	42.1	33.3	34	37.6
Total	94.7	89.4	85.8	86.3
Aromatic Carbon Selectivity (%)				
benzene	12.4	19.6	25.6	33
toluene	31.2	34.3	37.8	33.7
xylenes	22.4	18.9	16.9	10.2
Ethyl-benzene	1.6	2.7	1.4	0.8
styrene	2.5	2.4	1.1	0.6
phenol	4.8	5.2	4	2
benzofuran	6.2	1.8	1.6	3.2
indene	0.9	1.2	0.9	0.1
naphthalenes	18.2	14.0	10.7	16.5
Olefin Carbon Selectivity(%)				
ethylene	34.3	42.5	42.4	43.7
propylene	51.9	49.1	44.4	41.7
Butene	3.2	2.6	10.2	3.4
Butadiene	10.5	5.7	3	4.2
A+O Carbon Yield/ Theoretical A+O Carbon Yield(%)				
	29.3	42.7	23.8	32.5

Compare to the change in aromatic yield, the yield change of gas product changes are much smaller. Olefin yield does differ much for both catalysts although Ga/ZSM-5 are known for promoting olefin aromatization. It might indicate that some sort of thermodynamic equilibrium exist for olefin production. Also, CO yield decrease when converting over Ga/ZSM-5 compare to ZSM-5 catalyst, while the other gas product like CO_2, CH_4 does not show much difference. The coke yield for Ga/ZSM-5 is smaller than ZMS-5 at 550^{o}C and comparable for both catalyst around 600 ^{o}C.

Another interesting point from table 5 is that aromatic yield peaks at different temperature for these two catalysts. For Ga/ZSM-5 catalyst, aromatic yield maximize at a lower temperature compare to ZSM-5 catalyst. These could due to multiple reasons. It is proven that 500-550^{o}C is preferable temperature range for Ga/ZSM-5 catalyst to promote olefin aromatization. So 550^{o}C is the temperature for Ga to work at its best efficiency. Another possible explanation is the alkylation reaction between the small aromatics and olefins to form larger aromatics, eg. benzene and ethylene alkylation to form ethylbenzene. Due to alkylation reactions are exothermic reaction, thermodynamic limitation will become important when the temperature is too high. In fact, ethylbenzene starts to decompose into benzene and ethylene around 600oC. So lowering the temperature could help preserve the larger aromatic products.

CHAPTER 4

OLEFIN RECYCLE FOR BIOMASS CONVERSION OVER GA/ZSM-5 CATALYST

4.1 Introduction

Catalytic fast pyrolysis is a technology that can convert the biomass into aromatic and olefins in a single step. The process generate products in three different phases, liquid phase products are aromatics(desired products), the solid phase product is the coke deposited on the catalyst, gas phase products are a mixture including olefins(mainly ethylene andpropylene), methane, CO, CO_2. Although small olefins like ethylene and propylene are important building blocks for chemical industry, it will be expensive to separate them both monetarily and from an energy standpoint. This situation calls for other methods to utilize the gas phase mixture. Two possibilities are installing an alkylation unit after the reactor or establishing an olefin recycle loop. Adding an alkylation unit could serve the purpose of combine smaller olefins like ethylene, propylene with aromatics to form heavier aromatics, eg, ethylene react with benzene to form ethylbenzene; thus increase the yield of aromatics by incorporating converting olefins into aromatics. The other method, olefin recycle loop utilizes the advantage of Ga/ZSM-5 catalyst which promotes olefins aromatization. The second method is the focus for this section.

Olefin co-feeding experiments are designed to investigate if an olefin recycle loop will increase the aromatic yield. These experiments, involves co-feeding various amounts of ethylene and propylene with biomass(the WHSV of biomass is kept constant at $0.35hr^{-1}$). These series of experiments provided information about how increasing the amount of olefins inside the reactor affect the overall yield and product selectivity, as well as the behavior of catalyst. According to the paper by Carlson et al, aromatic yield is increased with both co-feeding of propylene using

ZSM-5 catalyst. They also proved that propylene is more reactive towards conversion into aromatics, while co-feeding ethylene does not seem to significantly affect the aromatics yield. In fact, in co-feeding ethylene experiments, there is a net production of ethylene.

According to the previous experiment results, ethylene and propylene are two major olefin products from biomass conversion over Ga/ ZSM-5 catalyst, combined, they account for 90% of the olefin produced. Therefore, the co-feeding experiments are focused on ethylene and propylene.

4.2 Ethylene co-feeding with biomass Experiments

Table 7 shows the experimental results for co-feeding ethylene with biomass. The first column of the table shows the results when biomass is the only feed, and the last column of the section shows the results when only ethylene is fed. In all the experiments the temperature and WHSV of biomass are kept constant at $550^{o}C$ and $0,35hr^{-1}$. The ethylene to wood ratio is defined as the moles of carbon in ethylene to moles of carbon in wood.

Table 6: Detailed carbon yield distribution and product selectivity for aromatic and olefin species for co-feeding of wood and ethylene. Reaction conditions: Ga/ZSM-5 catalyst, temperature 550℃, pine sawdust WHSV 0.35hr^{-1}, He velocity 2.27cm/s and 30 min total reaction time.

Experiment Type	Wood	Wood+Ethylene Recycle			
Carbon Recycle Ratio[a]	0	0.05	0.12	0.19	∞[d]
Ethylene Conversion(%) [b]	NA	-11.21	6.76	9.21	38.31
Overall Carbon Yield (%)					
Aromatics	23.17	19.81	12.76	6.83	7.26
Propene+C4 olefins	8.9[c]	2.34	1.12	0.78	80.73
Methane	1.5	1.12	1.33	0.66	0
CO2	5.41	4.32	5.76	3.18	0
CO	17.15	17.89	20.65	22.22	0
Coke	33.25	45.66	55.98	64.25	12.01
Total	89.35	91.14	97.6	97.9	100
Aromatic Carbon Selectivity (%)					
Benzene	25.74	22.71	38.65	39.54	70.93
Toluene	33.99	35.95	37.98	38.34	26.13
Xylenes	23.77	15.58	12.55	12.47	0
Ethyl-benzene	3.31	1.84	1.1	1.51	2.94
Styrene	2.82	2.6	0.93	0.88	0
Phenol	1.26	0.74	0.15	0.82	0
Benzofuran	1.67	4.12	1.12	0.33	0
Indene	1.48	0.52	0.32	0.47	0
Naphthalenes	5.96	10.06	7.65	3.65	0
Propylene and C4 olefin Carbon Selectivity (%)					
Propylene	47.11	75.6	78.65	79.7	82.38
Butene	4.31	8.76	9.91	8.38	9.31
Butadiene	2.54	9.87	11.44	7.61	8.3

a: Carbon Recycle Ratio= (Moles of Carbon in ethylene feed)/ (Moles of Carbon in wood feed)

b:Ethylene Conversion = (Moles of ethylene in-moles of ethylene out)/ (Moles of ethylene enter in); if the conversion is a negative number, then there is net production of ethylene, if the conversion is positive number then there is net consumption of ethylene

c: including propylene

According to Table 7, co-feeding ethylene lower the aromatic yield compared to only biomass in the feed experiment. Furthermore, the larger the carbon recycle ratio of ethylene, the lower the aromatic yield. When the carbon recycle ratio of ethylene reaches 0.19, the aromatic yield drops to 6.83%. Olefin yields (including propylene, butane and butadiene) also decreases with ethylene addition rapidly. Both the aromatics and olefins are produced from the hydrocarbon pool on the catalyst, the low yield of both two species indicate low activity of catalyst during the reaction time. Among the other gas products, methane and CO_2 yield generally stay the same but decrease at a high carbon recycle ratio of ethylene. CO yield decreases as the carbon recycle ratio goes up. Also, it is notable that in ethylene co-feeding experiments; there is a net production of ethylene which may suggest ethylene is not being actively converted into back into aromatics. Instead of being a reactant, ethylene is a stable product in the co-feeding experiment.

There is an increase in coke formed on the catalyst, about 20-30% percent more; coke yield doubled when the carbon recycle ratio of ethylene reached 0.19. The dramatic increase in coke yield will cause the catalyst to deactivate even faster; this fact could be an important reason why aromatics yield drops when increasing the amount of ethylene co-feeding in experiments.

Besides the effect on the overall yield, the aromatic selectivity also changes in co-feeding experiments. When increasing the co-feeding ethylene amount, benzene and toluene selectivity increase significantly. The other aromatics products, eg xylene, styrene, phenol, benzofuran phenol and nathphlensdecrease with the increase of carbon recycle ratio. Ali and co-workers have shown that by impregnating Ga on the surface of ZSM-5, the promoted catalyst has a stronger adsorption energy for ethylene compare to unprompted ZSM-5. It is possible that there

is competition betweenadsportion of ethylene and biomass pyrolysis vapor for the surface of catalyst during the reaction. So when more ethylene is provided to the system, benzene and toluene become dominate aromatic products. This could also contribute to the reason why co-feeding ethylene decrease the aromatic yield.

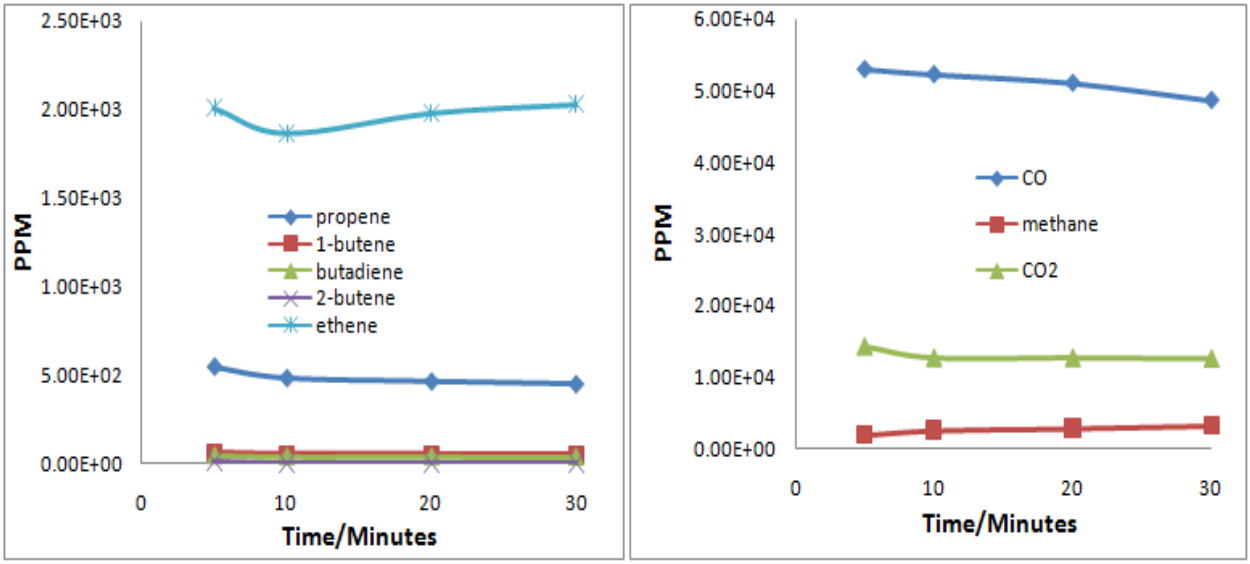

Figure 4: Time on stream for biomass coversion over Ga/ ZSM-5 with ethylene co-feeding((Reaction condition: Temperature 550, WHSV 0.35hr-1, He flow rate 1000sccm, ethylene to wood ratio: 0.12)

The time on stream of concentration of gas products are presented in Figure 2. It can be seen that the concentration of ethylene first drops during the time period of 5-8 minutes then gradually increases afterwards. Considering that ethylene is provided to the reactor system, this trend could mean between the start of experiments and 8 minutes that some of ethylene is converted. After this time period, there is a net production of ethylene from biomass pyrolysis. This result could indicate that the catalyst activity is reduced greatly after 8 minutes. Propylene concentration shows a decreasing trend from the beginning. This is additional evidence that

catalyst loses its activity because propylene is produced from the hydrocarbon pools on the catalyst. CO concentration decreases with time.

4.2.1 Ethylene conversion over Ga/ZSM-5 Catalyst

Table 5 and Figure 2 have already shown that co-feeding ethylene has detrimental effects in both the product distribution and the catalyst behavior. In order to further study the effect ethylene's effect on catalyst, experiments in which only ethylene is the only feed are performed.

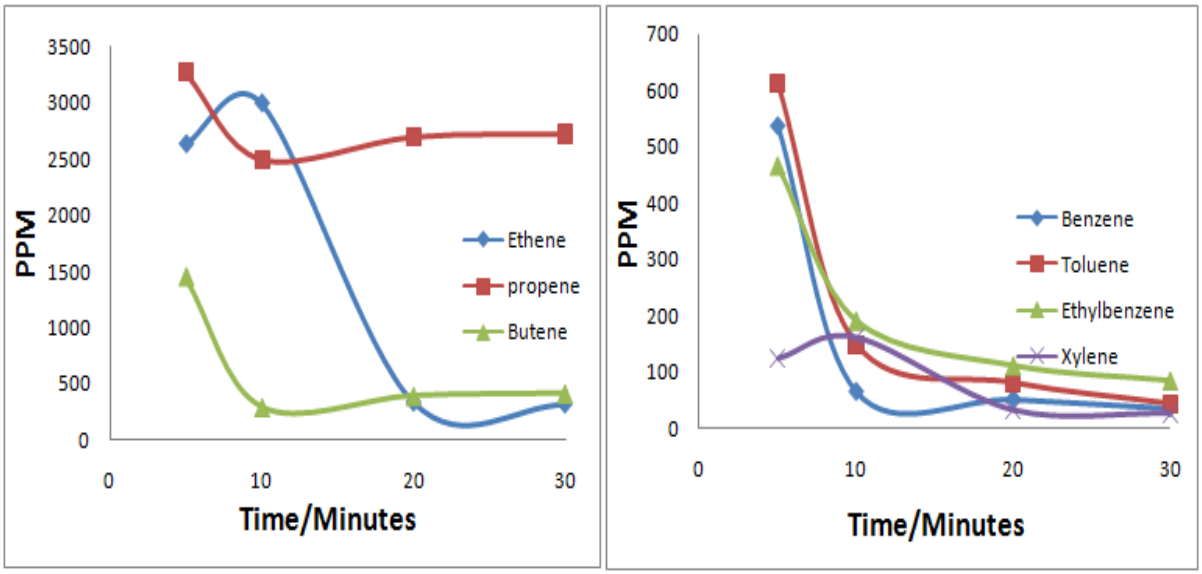

Figure 5: Product concentration as a function of time for ethylene conversion over Ga/ZSM-5 catalyst (Reaction Condition: temperature 550oC, 1000sccm He, ethylene concentration)

Figure 3 shows the time on stream for ethylene conversion over Ga/ ZSM-5 catalyst. The experiment is performed at 550^{o}C, the same temperature that the biomass conversion is operated at. During 30 minutes of experiments, the detected aromatics species are benzene, toluene, ethylbenzene. These results show that the Ga/ZSM-5 catalyst used for this research can covert olefins into aromatics. From Figure 4, that the aromatic products concentration drop dramatically

between 5- 10 minutes. After 10 minutes, the aromatic yields remain at a constant low level. This trend indicates that the Ga/ZSM-5 catalyst is losing its activity quickly in pure olefin. Also, from Figure 4, the other products from ethylene oligomerization: propylene and butane, their concentration first drops before 10 minutes then slowly increase, but their concentration changes are relatively small compare to aromatics. Considering about the carbon balance of the whole system, it can be deduced that after 10 minutes, most ethylene is directly converting to coke.

It is notable that in the ethylene conversion over Ga/ZSM-5 experiments, after 10 minutes, when the products aromatic concentration drop sharply, ethylene which is the reactant concentration also drops. This means although less aromatics are produced more ethylene is actually consumed. This trend could provide some insight about the coke formation on the catalyst during CFP. This results indicates that after a certain amount of coke is deposited on the catalyst, it will actually increase the rate of olefins converted into coke.. This could provide an explanation why in Figure 1, the time on stream of gas products in biomass conversion process, why the olefin concentration starts to drop after 10 minutes. The coke on the catalyst are actually making the olefins more prone to convert into coke.

The experiment with only ethylene as feed confirm the hypothesis that increasing the olefin concentration inside the reactor will make the catalyst lose its activity faster. Many researchs has shown that adding water into the experiments of olefins oligomerizations over Ga/ZSM-5 will help it remain stable. Water is a product from biomass pyrolysis. So it is possible during the co-feeding experiments, the reason why the catalyst appears to be more stable there is because of the presence of water.

4.3 Propylene co-feeding with biomass experiment

In CFP of biomass, propylene accounts for 4.5% of total carbon yield, about 40% of total olefin yield. Propylene and ethylene produced from biomass CFP is basically at 1:1 ratio. Therefore, propylene and ethylene are two important subject for olefin co-feeding study. The propylene to wood ratio is defined like in the ethylene co-feeding study, the moles of carbon of propylene to moles of carbon of biomass.

According to Table 6, co-feeding propylene with biomass is shown to increase the aromatic yield at low carbon recycle ratio. At the carbon recycle ratio of 0.16, the aromatic yield reaches the peak of 29.34%, which increase the aromatic yield by about 6% compare to experiments where biomass is exclusively the feed. Further increasing the propylene recycle ratio will cause the aromatic yield to decrease. Just like in ethylene co-feeding experiments, coke yield is much larger compare to experiments with only biomass in feed, and increase when more propylene is used in experiments. More coke formed during experiments could result in catalyst deactivates in a shorter time, this could be the reason why aromatics yield drops at high propylene to wood ratio. Besides aromatics yield, the olefins produced from the expeirments (ethylene, butenes) accounts for about 5-7% of total carbon yield. This number is much larger compare to ethylene co-feeding experiments, where the olefins produced generally is about 1-3% of carbon yield. Propylene is more active in converting in aromatics as well as other olefins on Ga/ZSM-5 catalyst compare to ethylene. The yield for CO, CO2, methane do not change much compare to experiments with only biomass. For all the propylene co-feeding experiments performed there is net consumption of propylene.

Table 7: Detailed carbon yield distribution and product selectivity for aromatic and olefin species for co-feeding of wood propylene. Reaction conditions: Ga/ZSM-5 catalyst, temperature 550℃, 0.35hr-1 wood WHSV, He velocity 2.27cm/s and 30 min total reaction time.

Experiment Type	Wood	Wood+Propylene Recycle				
Carbon Recycle Ratio[a]	0	0.15	0.16	0.24	0.26	0.57
Propylene Conversion[b]	NA	61.66	70.32	59.81	74.91	72.13
Overall Carbon Yield (%)						
Aromatics	23.17	27.02	29.34	25.06	27.65	22.07
Ethylene+C4 olefins	8.9[c]	5.16	5.61	6.21	6.67	5.98
Methane	1.5	2.06	2	2.27	2.55	2.13
CO2	5.41	7.76	4.32	6.32	7.21	5.66
CO	17.15	17.78	11.28	17.8	15.76	16.54
Coke	33.25	40.84	42.98	37.6	36.99	42.32
Total	89.35	100.62	95.53	95.27	96.83	94.7
Aromatics Carbon Selectivity (%)						
Benzene	25.74	15.13	18.65	17.07	16.2	15.9
Toluene	33.99	39.41	39.43	39.82	40.11	42.33
Xylenes	23.77	27.03	25.55	21.69	23.65	19.87
Ethyl-benzene	3.31	2.44	1.54	2.13	1.09	1.07
Styrene	2.82	5.02	6.01	3.87	6.47	5.87
Phenol	1.26	3.28	2.18	3.35	3.33	2.11
Benzofuran	1.67	0.78	1.11	0.59	0.85	0.94
Indene	1.48	1.49	0.98	1.15	2.09	1.95
Naphthalene	5.96	5.23	4.32	5.38	4.09	4.32
2-Methy Naphthalene	0	0.19	0.23	4.51	2.12	5.64
Ethylene+C4 olefin Selectivity(%)						
Ethylene	47.11	61.36	54	62.3	68	56.43
Butene	4.31	31.73	38.5	22.52	27.43	23.87
Butadiene	2.54	6.81	7.5	15.11	4.57	19.7

a: Carbon Recycle Ratio= (Moles of Carbon in propylene feed)/ (Moles of Carbon in wood feed)

b: Propylene Conversion = (Moles of propylene in-moles of propylene out)/ (Moles of propylene in)

c: including ethylene.

A decrease in benzene selectivity is observed while heavier aromatics like toluene and xylene are increasing with the concentration of propylene. This can be seen in the aromatic selectivity section from Table 7. As mentioned before in this article, toluene and xylene are assumed to be formed from the alkylation reaction on catalyst surface. Therefore, co-feeding propylene with aromatics will most likely promote alkylation reaction. Increase in the olefin aromatization reaction and alkylation reaction may be the two main cause for the increase of aromatic yield in co-feeding with propylene experiment. Besides the change in aromatic selectivity, there is also a sharp increase in butane yield. Butanes' yield accounts for about 22% of total olefin yield, which is about 10 times when converting biomass along.

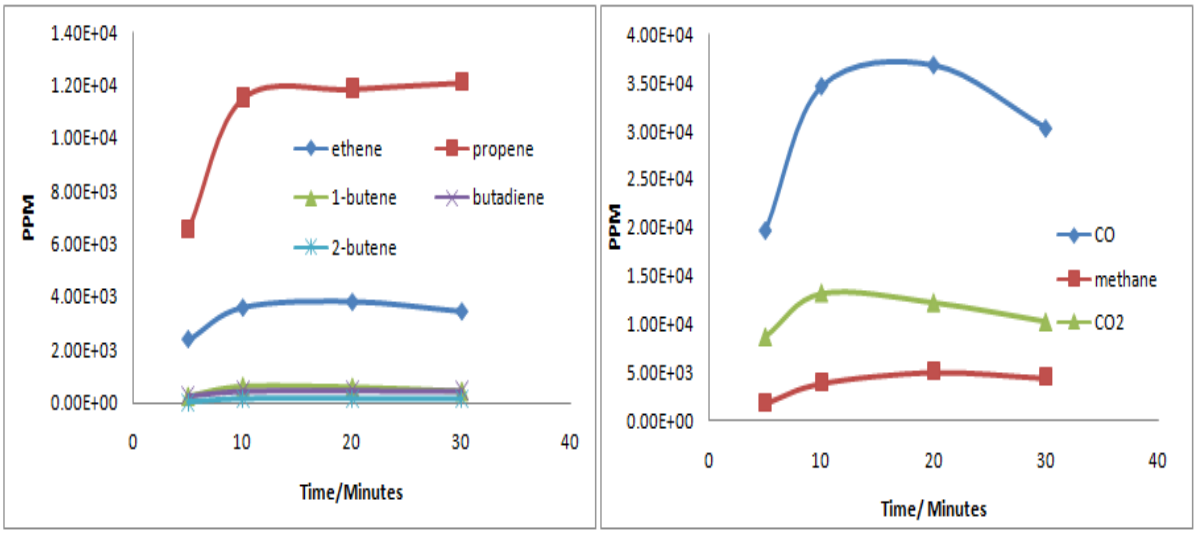

Figure 6: Gas phase products concentration as a function of time for biomass coversion over Ga/ZSM-5 with propylene co-feeding. (Reaction conditions: temperature 550oC, WHSV of wood 0.35hr01, He 1000sccm, propylene to wood ratio: 0.19)

Figure 6 shows the time on stream concentration for olefins, CO, CO_2 and methane for propylene co-feeing with biomass experiment. The reactant, propylene, concentration shows a sharp

increase from the start of experiments to ten minutes then remain steady afterwards. This increase in concentration means Ga/ZSM-5 is very active in converting propylene at the beginning. Ethylene concentration also goes up before 10 minutes then remain steady. Notable here ethylene is a product from hydrocarbon pools. The stable concentration of ethylene from 10 minutes to end could indicate that hydrocarbon pools formed in the experiments are stable in the low ratio propylene co-feeding experiments. CO and CO_2 concentration both show a increase in the beginning then drops after 10-15 minutes of experiments. These two gases products concentration trends are different from biomass conversion experiments.

4.4 Design of flow diagram for CFP process with olefin

As presented in the results above, olefin recycle for CFP do have the potential of increasing aromatic yield of the process. The previous results have pointed out that by recycling low ratio propylene, the aromatic yield will increase. On the other hand, recycle ethylene back into reactor will result in quick deactivation of catalyst and thus lower the aromatic yield. So it is desirable to separate ethylene from the recycle gas stream before it goes back into the reactor.

Based on previous results, CFP with olefin recycle is designed as the flow diagram presented below. The design is based on the reactor used in the experiments, but made two basic changes. First is the reactor no longer operates at batch condition but continuously. From the research of Carlson et al , the catalyst inside the fluidized bed can remain active less than 1 hour inside the fluidized bed reactor. So continuously operating the reactor will required constantly remove the spent catalyst into the regenerate system, and after regeneration, catalyst need to send back into reactor. Second requirement is recycle stream where allow gas products to flow back

into reactor. Inside this process, He is no longer used as the carrier gas for fluidized bed reactor, but the gas phase products from the process.

Figure 5 shows the proposed diagram for CFP process with olefin recycle. After simple pretreatment including grinding and drying, biomass is fed into the fluidized bed loaded with catalyst. This fluidized bed reactor is assumed to be loaded with Ga/ZSM-5 catalyst and operating at 550℃, WHSV of 0.35hr^{-1} for biomass which is the optimized working condition for Ga catalyst. Inside the reactor, the biomass undergoes a serious of reactions to convert into aromatics, olefins, CO, CO_2, CH_4 and coke. In order for the reactor to operate continuously, a regenerated system is connected to the reactor. During conversion of biomass, A stream of catalysts are sent into a regenerator from reactor to burn off the coke then sent back into reactor. The heat regenerated by burning off the coke on the catalyst can be used for heating the fluidized reactor

After the outlet stream leaves the reactor, it is sent into a separation system. First it went through a cyclone where small solid particles are separated from the steam. Then it went into a condenser where liquid products like aromatics are condensed and separated as water soluble stream are separated as waste stream. After the aromatics the condensers, there are olefins, CO, CO_2, and CH_4 left the in the stream. In order to achieve the maximum aromatics yield, ethylene is also removed from the stream. Thus, there is only propylene, butane, CO, CO_2 and CH_4 goes inside the recycle stream (stream 6). The flow rate of the recycle stream is determined as 4 times the minimized fluidized velocity for the fluidized reactor to ensure the reactor is operated inside the bubbling region. Gas products which do not go into recycle stream are burned as heating source for the whole system or other uses.

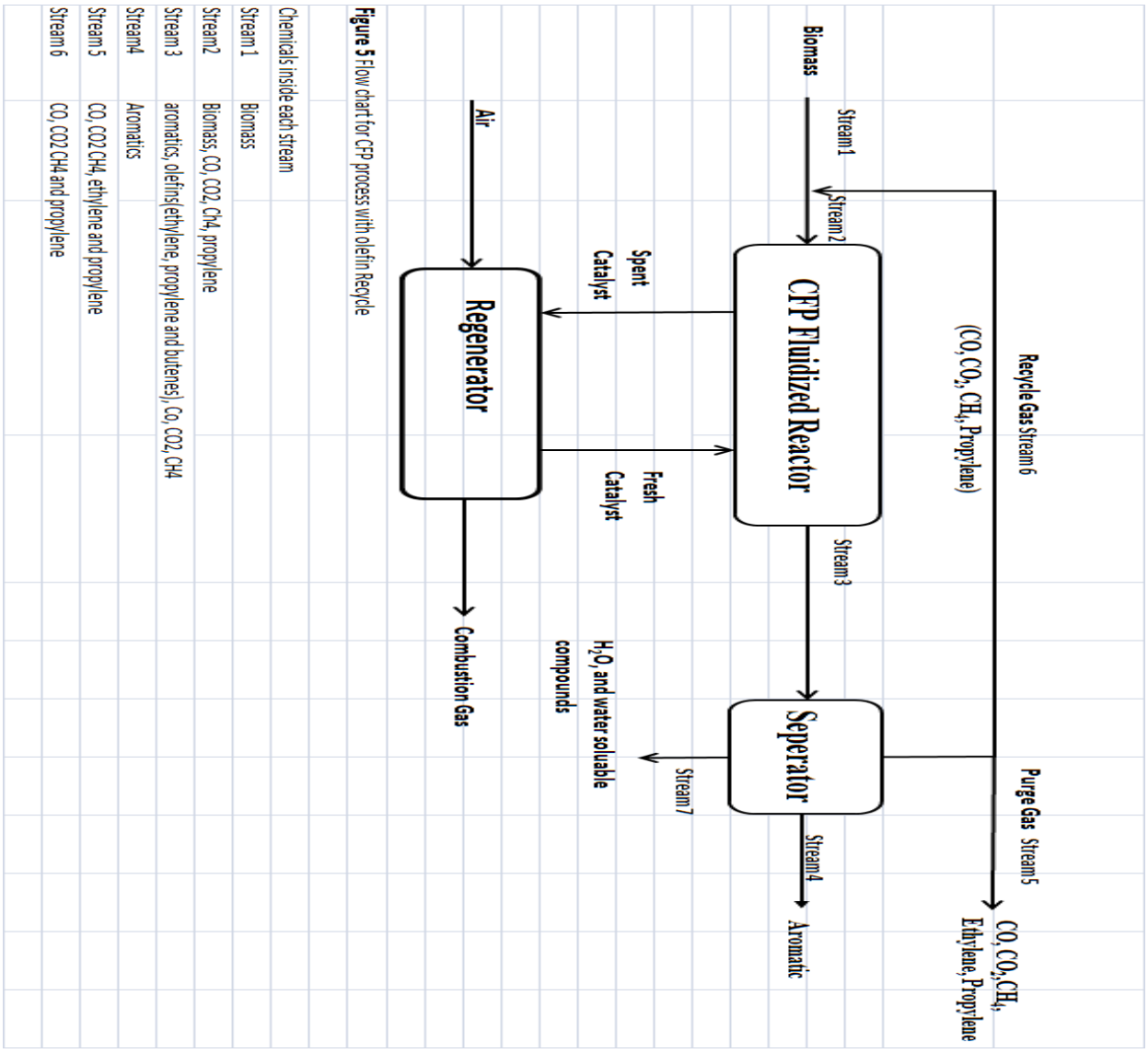

Figure 5 Flow chart for CFP process with olefin Recycle

Chemicals inside each stream	
Stream 1	Biomass
Stream2	Biomass, CO, CO2, CH4, propylene
Stream 3	aromatics, olefins(ethylene, propylene and butenes), Co, CO2, CH4
Stream4	Aromatics
Stream 5	CO, CO2 CH4, ethylene and propylene
Stream 6	CO, CO2 CH4 and propylene

Figure 7: Overall Diagram of CFP of Biomass with Olefin Recycle

4.4.1 Material balance for CFP process with olefin recycle

Based on the experiment results of biomass conversion and olefin co-feeding, the material balance of the whole system is calculated as below. The fluidized bed reactor is supposed to operate at 550^{o}C, the biomass WHSV are kept at 0.35hr^{-1}.

In order to calculate the aromatic yield for the CFP process with olefin recycle, three assumptions are made:

1. Assume propylene is the only chemical that will be reactive inside the recycle stream. So the CO, CO_2, CH_4, and butane inside the recycle stream will stay inert. Based on this assumption, if the fluidized bed reactor is operating at the same fluidized condition, replacing the fluidized gas He as the mixture of CO, CO_2, CH_4 will not change the product distribution.
2. Assume, the reacted propylene either forms aromatics or forms coke. As shown in Table 9, when co-feeding propylene with biomass, there is no obvious change in the yield of CO2 and Ch4, and a slight decrease in CO2. It can be assumed that main products of propylene oligomerization will be aromatics and coke.
3. The ratio of propylene turning into aromatics and coke are calculated based on the co-feeding experiment. In a certain propylene co-feeding experiments, the ratio of aromatics and coke produced from propylene is defined as below:

$$\frac{Propylene\ to\ aroamtics}{Propylene\ to\ coke} = \frac{Aroamtics\ yield(\ co-feeding) - aromatics\ yield\ (biomass\ along)}{Coke\ yield\ (co-feeding) - Coke\ yield(biomass\ along)}$$

For the propylene to biomass ratio not tested in co-feeding experiments, use linear calculation to get the aromatic to coke yield from propylene.

Based on the three assumption, the material balance for olefin recycle are calculated assuming that wood contains of 100 moles of carbon is feed into system. From the results, it can be shown that with olefin recycle aromatic yield could increase to 24.15%. If only produced from the CFP process is recycled back to the reactor, the propylene to wood ratio is very low, so the aromatic increase would be relatively small. Besides the increase in aromatic yield, the other advantage of olefin recycle is to allow gas products from CFP to replace the carrier gas He used in experiments.

Table 8: Material Balance for CFP Process with olefin recycle. (calculation are based on pine wood with 100 moles of carbons is feed into system). Reaction condition: 550^{o}C. Ga/ZSM-5 catalyst, WHSV of pine woods o.35hr^{-1}, assume that the recycle stream accounts for half of the total gas products out of reactor.

Material Balance							
Stream Line	1	2	3	4	5	6	Coke
Wood	100.00	100.00	0.00	0.00	0.00	0.00	0.00
Toluene	0.00	0.00	24.15	24.15	0.00	0.00	0.00
Ethylene	0.00	0.00	4.53	0.00	4.53	0.00	0.00
Propylene	0.00	3.90	5.86	0.00	1.95	3.90	0.00
CO	0.00	34.30	51.45	0.00	17.15	34.30	0.00
CO_2	0.00	10.82	16.23	0.00	5.41	10.82	0.00
CH_4	0.00	3.00	4.50	0.00	1.50	3.00	0.00
H20	154.00	0.00	0.00	0.00	0.00	0.00	0.00
H_2	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Coke	0.00	0.00	0.00	0.00	0.00	0.00	34.68
sum(mole):	89.37						
Carbon Balance							

4.5 Characterization of catalyst

The characterization of the catalyst is carried out on the catalyst which has undergone 28 complete reaction and regeneration cycle. For every cycle, the catalyst is first heated to 600℃ in He gas flow,then react with biomass for 30 minutes. After the reaction, the catalyst is purged for 30 minutes inside the He flow. In the final step, the catalyst is calcined at 600℃ to regenerate for 3 hours. During the 28 reaction cycles, pine wood is the only biomass tested in the experiments. And the catalyst activity remains stable throughout the 28 reaction cycles.

Table 9: Summary of overall reaction time

Reaction cycles	Contact time with biomass	Overall time in reaction-regeneration cycle
28	14hr	182hr

4.5.1 Elemental analysis

Table 9 shows the elemental analysis report on the catalyst. There are two purpose on doing elemental analysis for the catalyst. First is that whether Ga could be lost during experiments. As mentioned before in the experiments section, the 2%(weight) Ga is added to the catalyst by wetness incipient method, the Ga is not incorporated into the frame structure of the zeolite catalyst. The second is there are many trance metals inside biomass. Some of the metals could actually act as catalyst itself to some undesired reactions. Besides this effect, there are also concerns of trace metals deposited on the catalyst to poison it.

Table 10: Elemental analysis for fresh and spent catalyst

	Fresh Catalyst	Spent Catalyst
Element Present		
Gallium(wt/%)	2.09	1.89
Potassium(wt%)	0	0.401
Magnesium(wt%)	0.169	0.183
Calcium(ppm)	339	873
Manganese(ppm)	<47	72

As it can be seen in table 9, the amount of Ga is drop slightly from 2.09% to 1.89%. This slight decrease indicates that the Ga added to the zeolite catalyst by wetness incipient is stable for the high temperature and the time in contact with biomass and air flow. Four common trace metals from biomass: potassium, magnesium, calcium and manganese are also tested in the

elemental analysis. Elemental analysis results indicates that there are deposits of all four metals on catalyst after 28 reaction cycles, especially potassium. The catalyst used for elemental analysis are all thoroughly calcined, this findings shows that some of the trace metals can not be removed by just calcining the catalyst at high temperature. Although there are trace metals deposited on the catalyst, but the catalyst activity does not show much change in 28 reaction cycles could prove that these 4 metals does not poison the catalyst.

4.5.2 Alumina-TPD

To study show the reaction cycles affect the active sites on the catalyst. Alumina-TPD is performed on both the fresh and regenerated catalyst. Figure 6 shows the TPD results. Both catalysts have two peaks, one around 275 and one around 500. The peak at the low temperature may indicate the number of weak Lewis acid sites, where the alumina is weakly bounded on the catalyst. Correspondingly, the peak centered at the higher temperature may accounts for the sites of Bronsted sites, where the alumina is more strongly bounded on the catalyst. There is an obvious decrease in the Lewis sites while there is a slight increase for the Bronsted sites in spent catalyst compare to fresh catalyst. Overall the acid sites on Ga/ZSM-5 decrease after 28 reation cycles. The increase in Bronsted sites could be related to the lost of Ga through the experiments. According the research of Yu-ting, adding Ga to the catalyst will result in the decrease of Bronsted. It is possible that by losing Ga, the Bronsted sites on the catalyst are again revealed on

the surface.The total number of both acid sites are show in table 10.

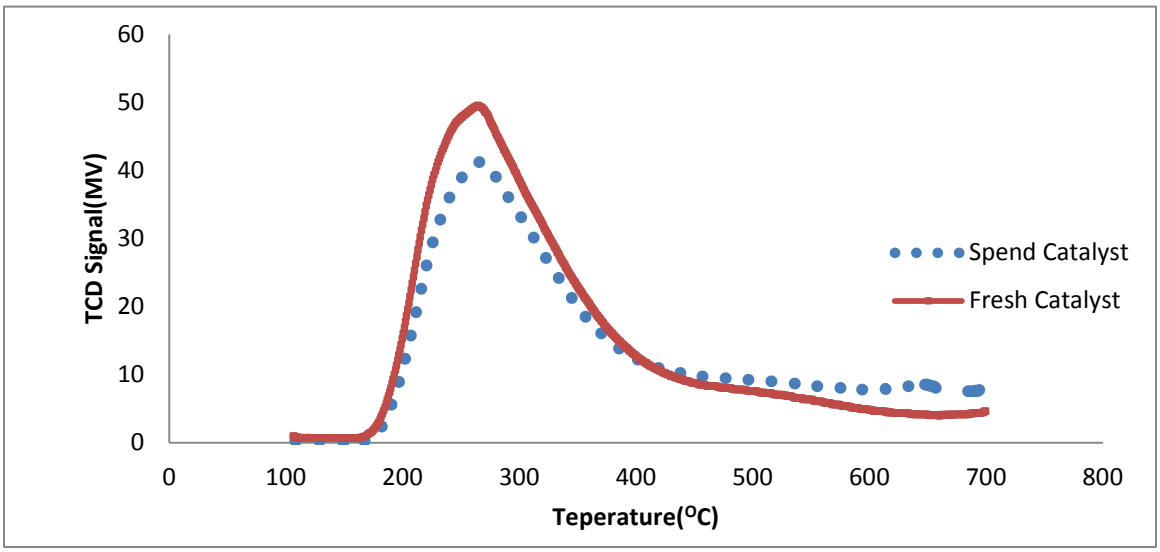

Figure 8: Alumina TPD for regenerated and fresh Ga/ZSM-5

Table 11: Total acidity of the fresh catalyst and the catalyst after 28 reaction-regerneration cycles

	Fresh catalyst	Spent Catalyst
Total acidity/nmol NH3 per gram of catalyst	0.44	0.30

4.5.3 XRD

XRD analysis is performed to study the crystal structure change of the fresh catalyst and the regenerated catalyst after 28 reaction cycles. Both catalyst are calcined at 600 ^{o}C for 3 hours to H-form products and to be sure Ga are preserved in Ga_2O_3 forms. In Shiyan's paper, they provide the XRD figure of ZSM-5 catalyst calcined at the same condition. Compare to the XRD figure of un-modified ZSM-5 catalyst, it can be seen that both the modified and un-modified

catalyst shows the similar peak pattern. The lack of extra peak for crystallinedGa compounds could mean that the Ga_2O_3 is neither highly dispersed on the ZSM-5 catalyst surface or is in an amorphous form.

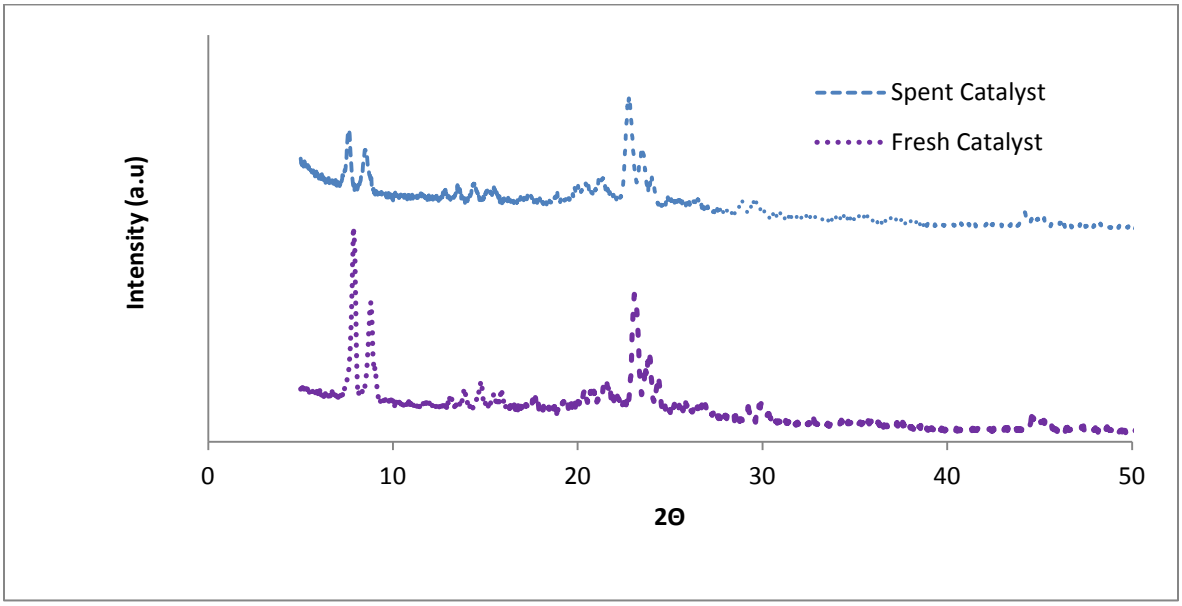

Figure 9: XRD for regenerated and fresh Ga/ZSM-5 catalyst

According to figure 9, compare to fresh catalyst, the regenerated catalyst shows some decrease in the intensity of the low angle reflection of XRD. It may indicate decrease crystallinity of the ZSM-5 catalyst. This could due to multiple reasons. One is water act with ZSM-5 catalyst at high temperature could cause it to lose crystallinity and water is a nature product of biomass pyrolysis. Also, there is small shift of the peaks between the fresh catalyst and regenerated catalyst. The peak shift in XRD usually indicates the variation of the dimension of unit cell which may due to the dealumination. The XRD pattern shows the crystal structure undergoes some changes after 28 reaction cycles.

CHAPTER 5

ALKYLATION UNIT FOR BIOMASS CONVERSION OVER GA/ZSM-5

5.1 Thermodynamic Considerations

In order to choose the appropriate temperature range for alkylation experiments, we first calculate the thermodynamic constants for all the reactions; the results are shown in Figure 3. From the calculation, we can see at high temperatures, above 550℃, all the alkylation reactions become thermodynamically impossible. So in the CFP fluidized bed (whose the operating temperature is 600℃),ethylbenzene, cumene, cymene and ethyltoluene decompose into aromatics and olefins. It could explain why there is little ethylbenzene inside the CFP products. So in order to alkylate the aromatics and olefins, we need to operate at lower temperatures, below 550℃.

All the alkylationreactions are exothermic, so the equilibrium favors non-alkylated forms with increasing temperatures. The formation of ethylbenzene is not favorable compared to other alkylation products, but this reaction is less thermally sensitive compared to the other reactions. At low temperatures, below 300℃the thermodynamic constant of toluene, cymene and cumene is much larger than ethylbenzene formation. But as the temperature increases to 400℃, the equilibrium constant of each reaction becomes close to each other.

So, based on thesecalculations, we chose 300 to 450℃ as the experimental temperature range. Above 500℃, cymene and cumene formation will not happen, below 300℃, ethylbenzene formation is negligible compared to other reactions, also, the reactions may be too slow.

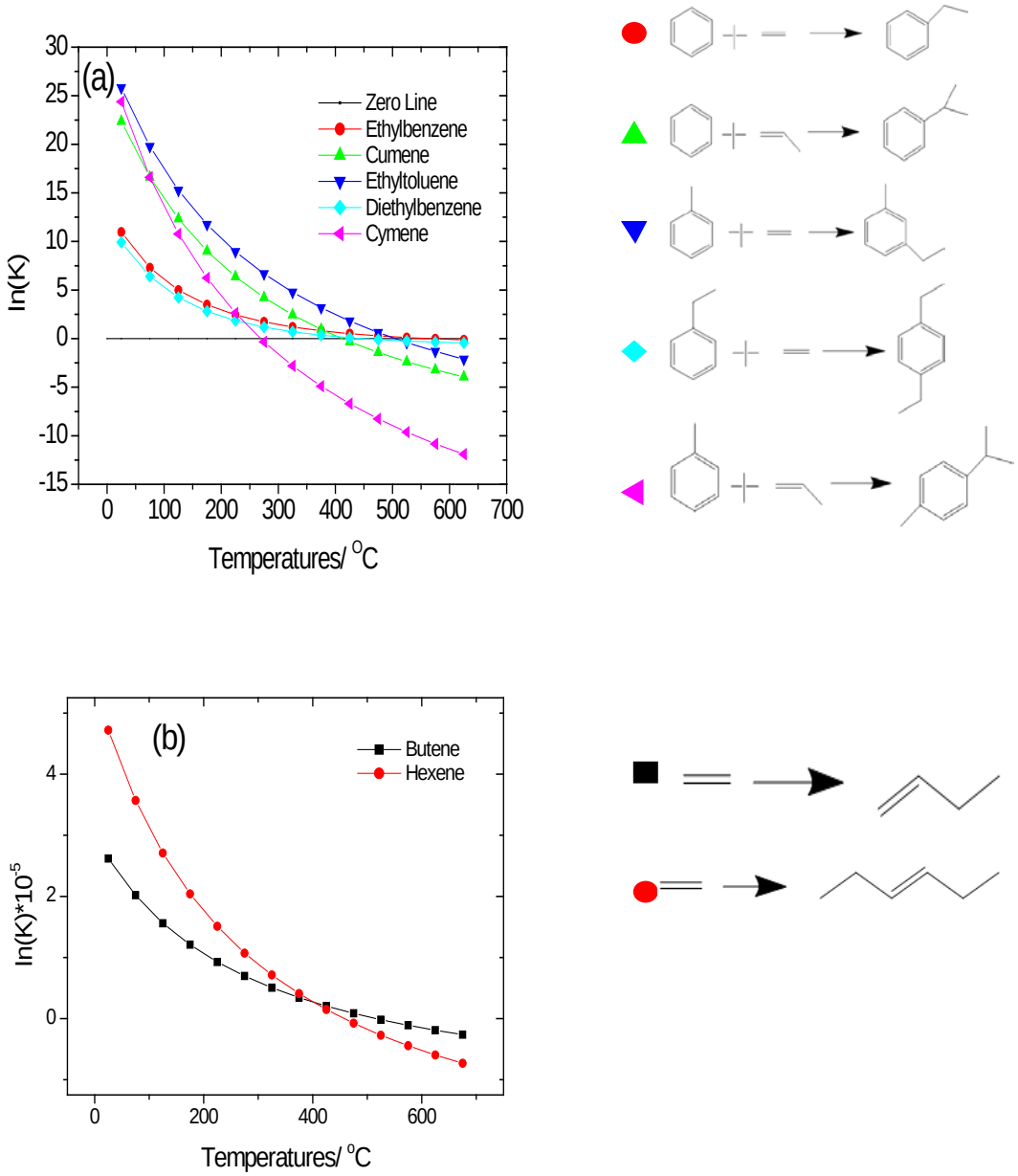

Figure 10: Calculated ln(K) as a function of temperature (a)Benzene and toluene alkylation with ethene and propene (b)Etheneoligomerization to form butene and hexene

5.2Benzene Alkylation at Different Temperatures with ZSM-5 Catalyst

After choosing 300-450℃ as the experimental temperature, we first test ZSM-5, Beta and Y zeolite in a feed containing benzene and ethene at different temperatures.

All three catalysts are stable at chosen temperature for alkylation experiment. Figure 4 shows the time on stream concentration of reactants and products for the reaction ofethene and benzene over ZSM-5 at 400℃. From the figure we can see the catalyst is very stable during the 1hr experiment. Although coke is deposited on the catalystduring the experiment, the concentration for both reactants and products don’t vary much according to time. Also, all the experiments with ZSM-5, Beta and Y Zeolite are performed on the same respective catalyst batches, so no permanentpoison for the catalyst is observed.

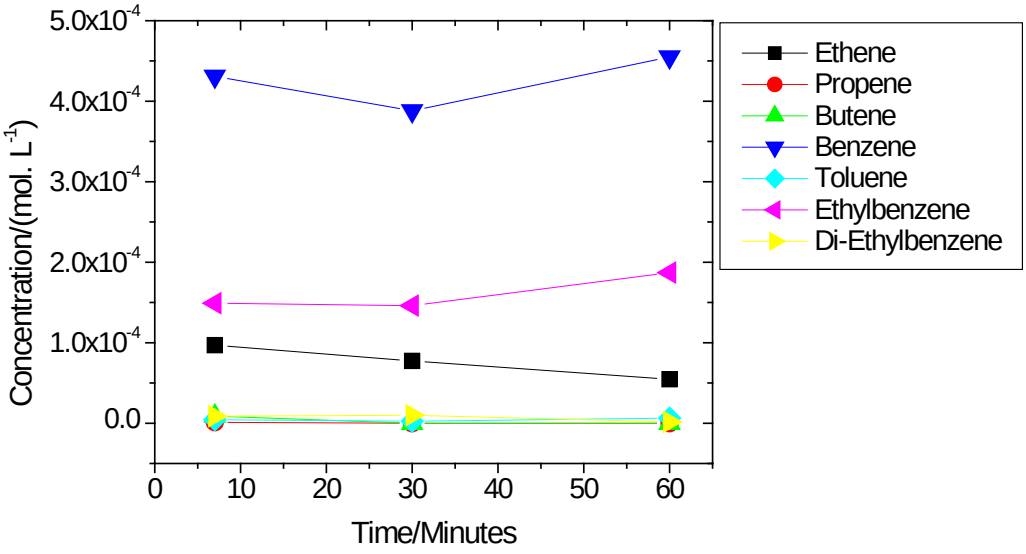

Figure 11: Time on stream concentration of reactants and products for benzene and ethene alkylation over ZSM-5 (experiment conditions: total pressure, 1 atm; temperatures 400℃; $WHSV_{benzene}$=1.52hr^{-1}; $WHSV_{ethane}$=0.55$hr^{-1;}$ B /E mole ratio=1:1; ethene partial pressure 0.00987atm, reaction time=1 hr)

Figure 5 shows the reactants conversion and products selectivity for ZSM-5 catalyst inside benzene and ethene feed at different temperatures. There is a huge rise in conversion from 250 to 300℃. At low temperatures, the reaction and transport rates are too slow. The conversions for ethene and benzene are stable between 300-400℃; the converstion for etheneis around 55%, benzene is around 20%. The conversion of ethene is higher than benzene may be due toetheneoligomerization with itself, which is responsible for the formation of coke,butene and propene.Also, the conversion low sensitivity to temperature from 300 to 400℃ might indicates that diffusion is the major limit for atmosphere pressure alkylation with ZSM-5. The conversion for both ethene and benzene drop dramaticallyas the temperature rise over 400℃. The decrease of conversion of benzene and ethylene from 400℃ to 450℃may result from the thermodynamic

limit for the alkylation reaction.

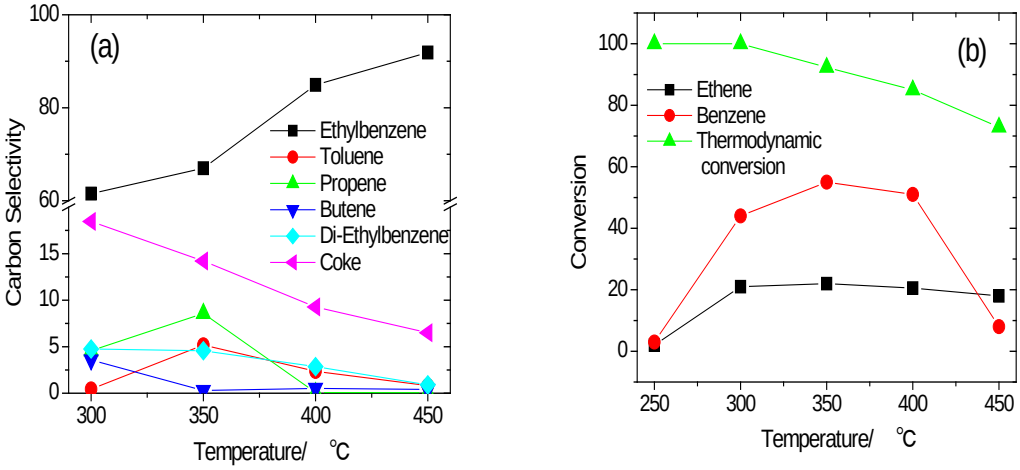

Figure 12: Reactant conversion and product selectivity for benzene alkylate with ethene as a function of temperatures over ZSM-5(reaction conditions: total pressure, 1 atm;$WHSV_{benzene}=1.52hr^{-1}$; $WHSV_{ethane}=0.55hr^{-1;}$ B/E mole ratio=1:1; Ethene Partial Pressure 0.00987atm, Reaction Time=1 hr) (a)Product Selectivity; (b)Conversion of reactants

Side products observed in the experiment are: propene, butene, toluene, and di-ethylbenzene. Propene and butene are formed by protonated etheneself-oligomerization, which occurs when there are not enough nearby aromatics species. The time on stream concentration shows that propene and butene concentrations drop with time, it may even disappear after 30 minutes. Di-ethylbenzene is formed by ethylbenzene continuing to react with ethene.

The selectivity of the ethylbenzene rises within the range of temperatures examined ([insert range here]), from 61.53 to 91.88%.The selectivity for ethylbenzene rises because: first at high temperatures 400℃, no propane or butane is observed. Rise in temperatures could increase the speed of diffusion of aromatics. Second, the coke amount formed on the catalyst reduces with the

rise of temperatures, (300℃, 18.45%, 400℃, 9.27%).

5.3 Benzene and Ethene Alkylation with Beta Zeolite at Different Temperatures

Figure 6 shows the alkylation experiments on Beta zeolite catalyst. Beta zeolitecatalyst is a good catalyst for liquid phase alkylation of ethylbenzene. Beta zeoliteshows high conversion for benzene and ethene but the selectively for ethylbenzene is low due to high rate of coke formation. Olefins alkylation with aromatics on zeolite catalyst iscommonlybelieved to follow a mechanism containing a carbenium ion intermediate. Olefins are excited by the zeolite catalyst to form carbenium ions. The reaction between carbenium ion itself and dealkylation of aromatics is responsible for coke formation. Beta catalyst's high activity for ethene at atmosphere pressure may cause the large amount of coke formed on the catalyst. The highest conversion for Beta catalyst is observed at 350℃, for ethene it is 69%, for benzene is 54%. The decrease in conversion from 350 to 400℃may result from the deactivation of catalyst due to large amount of coke formed on the catalyst.

The side products observed in alkylation experiment with Beta catalyst are propene, butene, toluene, xylene, Di-ethylbenzene. The selectively for ethylbenzene reduces with temperature.The amount of coke formed increases rapidly with the increase of temperature.

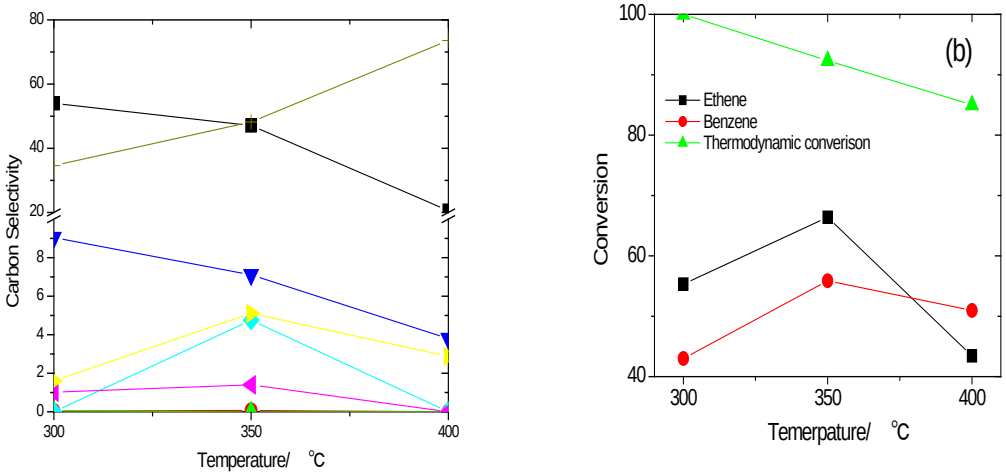

Figure 13: Reactant conversion and product selectivity for benzene alkylated with ethene as a function of temperatures over beta zeolite(Reaction conditions: Total pressure, 1 atm;$WHSV_{benzene}$= 1.52hr^{-1}; $WHSV_{ethene}$=0.55$hr^{-1;}$ B/E mole ratio=1; Ethene Partial Pressure 0.00987atm, Reaction Time= 1 hr) (a) Product Selectivity (b) Reactant Conversion（■Ethylbenzene●Propene ▲Butene▼Toluene ◆Ethyltoluene◀Xylene ▶Di-ethylbenzene┼Coke

5.4 Benzene and Ethene Alkylation with Y Zeolite at Different Temperatures

Figure 7 shows the alkylation of ethene and benzene on Y zeolite. Like Beta zeolite, Y zeolite is mainly used as a liquid phase catalyst for the alkylation ofethylbenzene. At atmosphere pressure, Y zeolite shows a low conversion for benzene and ethene at the range of temperatures examined. The conversion for both rises with temperature. At 400℃, the conversion for ethene is 41% while the conversion for benzene is 19%. The conversion is far below the thermodynamic limit.

The side products observed during experiments are toluene, ethyltoluene and di-ethyltoluene. Compare to ZSM-5 and Beta zeolite, there is no propene orbutene observed during

the experiments.This may indicate Y zeolite does not readily activateethene into the carbenium ion, which may explain the low conversion for ethene and benzene. Also, Y zeolite is the only catalyst which produced ethyltoluene. According to Figure 7, the most important side product for Y zeolite is toluene, about 8-27.56% formed in the reaction, Also, freshly formed toluene is very active; about 40% of it reacts with ethene to form ethyltoluene, so there is a total about 20% ethyltoluene formed during the reaction. So Y zeolite may be a good catalyst for producingethyltoluene at atmosphere pressure.

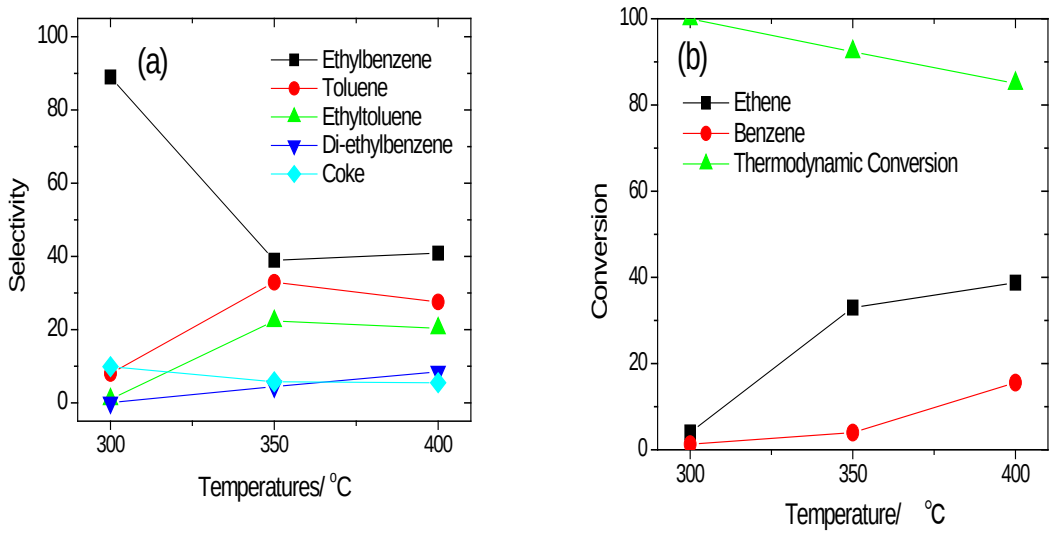

Figure 14: Reactant conversion and product selectivity for benzene alkylate with ethene as a function of temperatures over Y zeolite(Reaction conditions: Total pressure, 1 atm;$WHSV_{benzene}$= 1.52hr^{-1}; $WHSV_{ethene}$=0.55$hr^{-1;}$ B/E mole ratio=1; Ethene Partial Pressure 0.00987atm,Reaction Time, 1 hr) (a) Products' Selectivity ; (b) Reactants' Conversion

From the experiment above, ZSM-5 shows the best selectivity and activity for ethene and benzene alkylation. For Beta zeolite, the conversion for ethene and benzene is high, however there is too much coke formed. For Y zeolite, the selectivity forethylbenzene is low; too much

toluene formed during the experiments. Also, the best temperatures for ZSM-5 and Y zeolite is400℃, while Beta zeolite is 350℃.

5.5 Benzene alkylation on three Catalysts with the presence of Toluene

There is 4.37C% toluene inside the CFP products which is not removed by the separation unit. Toluene could alkylate with ethene to form ethyltoluene at 300 to 400℃ range. In order to study how toluene affects the benzene and ethene alkylation, we add toluene into the feed for the alkylation experiment with the three kinds of zeolite catalyst. The experiment temperature is chosen to be the best temperature for ethene and benzene alkylation for three catalysts ([temp°C]). The experiment pressure is chosen to be atmosphere pressure.

Table 4 shows the results for alkylation experiment with toluene in the feed.

Table 12: Product Distribution and Reactant Conversion for Alkylation Experiment with ZSM-5, Beta and Y zeolite for Benzene, Toluene and Ethene in the Feed

Catalyst type	ZSM-5		Beta Zeolite		Y Zeolite	
Feed Ratio[a]	B:E (1:1)	B:E:T (1:1:0.9)	B:E (1:1)	B:E:T (1:1:0.9)	B:E (1:1)	B:E:T (1:1:0.9)
Conversion (%mol)[b]						
Ethene	51.00	41.90	66.39	40.34	37.76	32.57
Benzene	20.56	13.21	59.88	45.72	15.58	7.54
Toluene	NA	9.78	NA	48.1	NA	2.85
Carbon Selectivity (%mol)						
Propene	0.07	ND	0.09	ND	ND	ND
Butene	0.52	ND	ND	ND	ND	ND
Toluene	2.36	NA	9.05	NA	26.79	NA
Ethylbenzene	84.91	62.79	42.44	14.51	39.61	44.22
Ethyltoluene	ND	22.12	ND	15.19	19.74	49.69
Xylene	ND	ND	6.05	8.76	ND	ND
Di-ethylbenzene	2.82	2.79	8.47	2.24	8.47	ND
Coke	9.27	12.29	34.09	59.30	5.48	6.09

Note: Reaction Condition: for ZSM-5 and Y-Zeolite Temp: 400℃, for Beta Zeolite Temp: 350℃, Catalyst Weight: 0.2556g, Benzene Molar Flow: $8.248*10^{-8}$mol/h, Ethene WHSV: 0.55hr^{-1}, Benzene WHSV: 1.52 hr^{-1}.
a: Molar ratios; B for Benzene, E for Ethene, T for Toluene
b: Conversion obtained by collecting data at 7, 30, 60min time on stream

It can be seen from the table, that after adding toluene, the conversion for benzene and ethene with all three catalysts decrease. ForZSM-5, the conversion for ethene reduces from 51% to 41.9%, also, for benzene it reduces from 20.56% to 13.21%. There is competitive adsorption between toluene with benzene on the catalyst and toluene can also competitively react with thecarbenium ion formed by the activated etheneon the zeolite catalyst. Toluene is more thermodynamically favorable to adsorb on zeolite catalyst.

After adding toluene, the selectivity for ethylbenzene reduces when using ZSM-5 and Beta zeolite, while it increases slightlywith Y zeolite. Ethyltoluene is observed for all three catalysts.

So all three catalyst can catalyze the alkylation of ethene with toluene at atmosphere pressure. For ZSM-5, the selectively reduces from 84.91% to 62.79%. Additionally, the coke amount for all three catalyst increases after adding toluene,,especially for Beta zeolite; the coke amount increases from 34.90% to 59.30%. For Y zeolite, adding toluene in the feed produces more ethyltoluene than ethylbenzene. It indicate that Y zeolite is more selective to ethyltoluene at atmosphere pressure, which is consist with the experiment with only benzene and ethene in the feed. Also, when toluene is added, there is no propane and butane observed during the experiment.

From the experiment result, ZSM-5 catalyst has the best selectivity for ethylbenzene after toluene is introduced into feed. For Beta catalyst, too much coke formed during the experiments, while Y Zeolite is more selective to ethyltoluene than ethylbenzene at atmosphere pressure.

5.6 Benzene alkylation with Xylene on ZSM-5

CFP products containaromatics which are mainly benzene, toluene and xylene, and in the jet fuel process, only water is separated from the feed in the separation unit. So we need a catalyst which could alkylate benzene, toluene with ethene and propene in the presence of xylene.

Here, we compare three experiment results: 1) only benzene and ethene in the feed; 2) benzene, toluene and ethene in the feed 3)???. The results are show in Table 4. All the experiments are performed on ZSM-5.

Table 13: Benzene Alkylation with 1) Ethene in the Feed, 2) Ethene, Toluene in the Feed, 3) Ethene, Toluene and Xylene in the feed over ZSM-5 at 400℃

Feed Ratio[a]	1)E:B (1:1)	2)E:B:T (1:1:0.9)	3)E:B:T:X (1:1:1:1)
Conversion (%mol)[b]			
Benzene	21.56	13.21	20.34
Ethene	51.00	41.90	43.95
Toluene	NA	9.78	3.40
Xylene	NA	NA	34.84
Distribution for Main Aromatic Product Distribution (%mol)			
Propene	0.07	ND	ND
Butene	0.52	ND	ND
Toluene	2.36	NA	NA
Ethylbenzene	84.91	62.79	56.31
Ethyltoluene	ND	22.12	27.63
Diethylbenzene	2.82	2.79	3.59
Coke	9.27	12.29	12.46

Note: Reaction Condition: Temp:400℃, Catalyst Weight: 0.2556g, Benzene Molar Flow: $8.248*10^{-8}$mol/h, Ethene WHSV: 0.55hr^{-1}, Benzene WHSV: 1.52 hr^{-1}.
a Molar ratios; E for Ethene, B for Benzene, T for Toluene
b Conversion obtained by collecting data at 7, 30, 60min time on stream

During theexperiment, no xylene alkylation products are observed. So xylene cannot alkylate with ethene under atmosphere pressure with the three zeolite catalysts. The conversion for benzene and ethene is slightly higher when xylene is added rather than whenonly toluene is added to the feed alone. This may be caused by the competitive adsorption of xylene with toluene while xyleneitself doesn't alkylate with ethene on zeolite catalyst under atmosphere pressure. Thermodynamically, xylene is more thermodynamically favorable to adsorb on zeolite than toluene.

After adding xylene to the feed, the selectivity for ethylbenzene is slightly lower than adding toluene to the feed alone, from 62.79% to 52.31%. Also, the selectivity for ethyltoluene

increases from 22.12% to 27.63%. The coke amount doesn't change much for adding xylene to the feed, about 12.46% of carbon goes into coke. There are no propene and butane formed in the reaction, just like the experiment with toluene and benzene in the feed. There's only trace amount of xylene alkylation products detected in the reaction, so almost no xylene alkylate with ethene.

From the experiment result above, we can see toluene have much more obvious effect on benzene alkylation than xylene.

5.7 Ethylbenzene Alkylation Experiments On CFP Products

From the above experiment we can see that ZSM-5 is the best catalyst among the three zeolite catalyst for benzene alkylation under the presence of toluene, so we choose ethylbenzene to be the catalyst for the alkylation fix bed after CFP fluidized bed.

Table 8 shows the product distribution comparison between the CFP process with the alkylation unit (Control Group) and With the Alkylation unit (Alkylation Group). During experiment, the separation unit before alkylation unit only separate water from the feed.

With the alkylation unit, the carbon yield for ethylbenzene rise from 0.08% to 3.59%, (0.76% to 25.22% for the selectivity out of all the aromatics). Meanwhile, the carbon yield for toluene, xylene and other aromatics does not change after adding the alkylation unit. So ZSM-5 catalyst shows high selectivity in alkylating benzene and ethene inside the CFP products.

CHAPTER 6

CONCLUSIONS

Catalytic fast pyrolysis is a technology to convert biomass into aromatics in a single step reactor. Gallium promoted ZSM-5 catalyst is shown to increase the hydrocarbon selectivity towards aromatics. Compare to ZSM-5 catalyst, the aromatic yield has increased by 40% in the process of catalytic fast pyrolysis of pine saw dust.

Reaction parameters like temperature, weight hourly space velocity, fluidized gas velocity could be used to tune the hydrocarbon selectivity as well as product distribution. Product distribution is a strong function of temperature and weight hourly space velocity, fluidized gas velocity has less apparent effect on the aromatic yield. Aromatic production is more preferable at high temperature($550^{o}C$) and low weight hourly space velocity ($o.35hr^{-1}$).

Gallium is introduced to the ZSM-5 by wetness incipient method. Gallium impregnated on ZSM-5 is stable during the catalytic fast pyrolysis of pine sawdust. After 28 reaction cycles, about 10% of Ga is lost. There are mineral impurities deposited on catalyst eg. Calcium, Magnesium, Potassium, Manganese. These trace minerals deposited on catalyst does not appear to alter catalyst performance for catalytic fast pyrolysis of biomass. After 28 reaction cycles, there is slight change in the zeolite crystal structures as well as its acidity.

Besides aromatics, the other products from catalytic fast pyrolysis of biomass include olefins, CO, CO2 and methane. Two possible ways to utilize the olefins and avoid the high expense to separate them from gas phase product mixture are:

1) recycle olefins back into reactor to convert into aromatics;

2) building an alkylation unit after reactor to promote the alkylation between olefins and aromatics.

Olefin co-feeding experiment results suggest that recycling ethylene and propylene back into reactor will change the product distribution. Recycle propylene back into reactor could increase the aromatic yield, at the same time, coke yield will increase too. Recycle ethylene will result in quick deactivation of the catalyst, therefore reduced the aromatic yield. There is a possible competition between the ethylene and oxygenates from the biomass pyrolysis on the active sites of catalyst

Adding the olefin alkylation unit after the reactor with catalyst that has high selectivity and activity towards benzene and ethylene alkylation could result in possible process to produce ethylbenzene production from the biomass. From the three catalyst tested(Y zeolite, Beta Zeoltie and ZSM-5), ZSM-5 has the highest selectivity and activity towards benzene and ethylene alkylation. Because alkylation reactions are endothermic reactions, the alkylation unit will be best to operate lower temperature than the fluidized bed reactor.

With Ga/ZSM-5 catalyst, 43% of theoretical aromatics+ olefin yield is achieved. This study of catalytic fast pyrolysis of biomass over Gallium promoted catalyst points out that this technology has much potential to improve with the advance of catalyst and combined process design.

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